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A STUDY OF THE STRONTIUM AND BARIUM HALIDES AS COLUMN PACKINGS IN GAS-SOLID CHROMATOGRAPHY

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SUMMARY

The halide salts (chloride, bromide, iodide) of strontium and barium have been investigated as column packings in gas-solid chromatography. Various groups of organic compounds have been studied, their heats of adsorption calculated and models presented to explain their behavior on these columns. Sample size required to produce overloading generally increased with increasing anion size in the packing. Retention volumes generally followed boiling points; two compounds having the same boiling point a greater adjusted retention volume was noted for the more polar compound. Chain branching reduced retention volume. Adjusted retention volume increased as size of anion in packing increased.

INTRODUCTION

The most exhaustive work in gas-solid chromatography (GSC) has been carried out using charcoal, alumina and silica gel. Since 1960, however, considerable attention has been focused on the use of inorganic salts either in eutectic mixtures adsorbed on a solid support or as a pure salt adsorbed on a solid support[1-7]. In particular ŠOLOMON[6,7] carried out a comprehensive study which included the use of alkaline earth salts and alkali metal halides, carbonates and sulfates which gave an indication of the versatility of inorganic salts in gas chromatography for separating many organic systems. In 1964, ALTENEAU AND ROGERS[8] published their work on the use of the nitrate and sulfate salts of the ammonia and pyridine complexes of copper. Further an extensive study of the alkali chlorides and nitrates, using a variety of organic adsorbates, was done by GROB *et al.*[9].

More recent work in the area of GSC represented an extensive investigation into specific interactions affecting retention, thermodynamics and separation efficiencies, and correlations of aromatic substituent effects[10-14]. These studies led to a thermodynamic gas chromatographic retention index for organic molecules.

Because of the great potential selectivity of solids, GSC is especially desirable for the separation of isomers and high molecular weight compounds[6,7]. This selectivity,

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coupled with high column temperatures permissable prompted the present research dealing with an evaluation of the adsorptive properties of the barium and strontium halides (chloride, bromide and iodide) as column packings in GSC.

EXPERIMENTAL

Column preparation

The alkaline earth halides, with the exception of strontium iodide, were dehydrated in a muffle furnace at 400° using a nitrogen purge. Strontium iodide was dehydrated at 325° because higher temperatures results in slight decomposition and discoloration. After cooling in a vacuum desiccator, the halides were transferred to a dry box where they were ground with a mortar and pestle, sieved to 60/80 mesh, and packed into 6-ft. glass columns (O.D. 0.25 in., I.D. 0.23 in.) using vacuum and gentle tapping. 1/4 in. plugs of glass wool were used in both ends of the glass tubing. Silicon rubber plugs were then inserted into both ends of the packed columns. The columns were transferred directly to the chromatograph oven and conditioned for 24 h at 300° with a helium flow rate of 100 ml/min. It was often necessary to re-sieve and repack the columns after conditioning due to the formation of gas pockets within the column packings. Apparently the barium and strontium halides are very brittle and easily produce fines and pack tighter once carrier gas is passed through the column.

Sample syringes

One and ten microliter Hamilton syringes were used for all sampling.

Recorder

The recorder was a Leeds and Northrup Speedomax H with a 1 mV chart span.

Gas chromatograph

A modified Nester-Faust Anakro IA gas chromatograph equipped with a thermal conductivity detector was employed throughout the entire investigation. The gas chromatograph was modified to increase sensitivity of response and temperature control.

Inorganic salt packings

Barium and strontium chloride were obtained from Baker Chemical Co., Phillipsburg, N. J. and were Baker Analyzed quality. Barium bromide, strontium iodide and strontium bromide were obtained from Rocky Mountain Research Company, Denver, Colo. Barium iodide was acquired from the Fisher Scientific Company, Pittsburgh, Pa. The latter four halides were reagent grade. All of the salts were purchased as the di-hydrate.

Samples

All organic chemicals used for this investigation were supplied by Chemical Service Inc., Media, Pa. and were chromatographic grade.

Experimental conditions

The retention time for each sample was obtained in triplicate on each column at temperatures of 170, 200, and 250° for the barium halides and 150, 200 and 250° for the strontium halides. Only those values which were reproducible within ± 0.1 sec were considered acceptable. The injection port temperature was 250° and the detector temperature was 360°. Carrier gas flow for the strontium halide columns was 40 ml/min and that for the barium halide columns was 60 ml/min. 0.1 μl samples were used throughout the investigation.

RESULTS AND DISCUSSION

The samples used throughout this investigation can be classified into three main groups, *i.e.*, alcohols, carboxylic acids, and isomeric aromatic compounds. Heats of adsorption for the above compounds have been tabulated in Table I and Table II. Table III shows a selected group of aromatic compounds along with their adjusted retention volumes and heats of adsorption on the barium chloride column.

Alcohols

The alcohols shown in Table I are listed in order of increasing boiling point. Certain trends are immediately obvious. In all cases, as one proceeds from the chloride to the bromide to the iodide column for a specific cation, the heat of adsorption (—ΔH_a) increases. It can be seen from the data for the C$_1$ to C$_5$ straight chain alcohols, that adsorption is not merely a function of boiling point as one might anticipate. It appears that dipole moment and possibly the formation of weak hydrogen-like bonds would best explain our results. The inversion of the methanol and ethanol

TABLE I

HEATS OF ADSORPTION FOR ALCOHOL AND CARBOXYLIC ACID SAMPLES(kcal/mole)[a]

Sample	*b.p.(°C)*	*Dipole moment*	*Column*					
			SrCl$_2$	*SrBr$_2$*	*SrI$_2$*	*BaCl$_2$*	*BaBr$_2$*	*BaI$_2$*
Alcohols								
Methyl	64.6	1.68	0.78	1.26	6.22	6.71	7.80	a
Ethyl	78.5	1.71	1.51	3.69	8.59	4.81	5.21	a
Propyl	97.0	1.66	1.27	1.39	4.98	1.53	a[b]	a
n-Butyl	117.0	1.67	2.73	3.41	7.53	2.80	a	a
n-Amyl	138.0	1.73	3.53	4.12	8.52	2.81	a	a
Isopropyl	82.0	1.59	1.21	1.26	4.67	1.36	10.17	a
Isobutyl	108.0	1.64	1.79	2.86	7.52	1.23	a	a
sec.-Butyl	99.0	N.A.[c]	1.72	3.60	5.45	0.82	a	a
tert.-Butyl	82.8	N.A.	1.66	1.80	3.10	0.58	a	a
Isoamyl	131.5	N.A.	3.35	3.65	6.29	1.76	a	a
tert.-Amyl	102.0	N.A.	1.95	3.63	5.49	0.94	a	a
Acids								
Formic	100.7	1.52[d]	0.28	2.22	a	2.70	3.61	a
Acetic	118.1	1.69	0.43	2.39	a	2.81	a	a
Propionic	141.0	1.76	1.22	2.95	a	5.61	a	a
Butyric	162.5	N.A.	2.21	3.36	a	7.03	a	a
Isobutyric	154.0	N.A.	1.21	2.39	a	4.22	a	a
Valeric	182.5	N.A.	a	a	a	7.36	a	a

[a] All results are negative.
[b] a = unable to calculate due to rounded peak tops and excessive tailing.
[c] N.A. = not available.
[d] Dipole moment = 1 for dimer at 150°.

TABLE II

HEATS OF ADSORPTION FOR AROMATIC SAMPLES(kcal/mole)[a]

Sample	*b.p.*(°C)	*Dipole moment*	*Column*					
			$SrCl_2$	*$SrBr_2$*	*SrI_2*	*$BaCl_2$*	*$BaBr_2$*	*BaI_2*
Benzene	80.0	0.00	0.92	1.71	2.19	0.00	0.10	5.03
Toluene	110.6	0.37	1.46	2.80	4.15	0.00	2.13	6.56
Mesitylene	164.0	0.00	3.13	5.56	7.29	2.80	6.92	a[b]
o-Xylene	144.4	0.62	2.28	2.67	7.16	1.11	5.62	8.92
m-Xylene	139.8	N.A.[c]	2.06	2.91	6.22	N.A.	N.A.	N.A.
p-Xylene	138.4	0.00	2.56	2.60	9.26	1.76	5.65	8.79
Cl-Benzene	131.0	1.70	1.33	2.03	2.49	2.11	6.46	6.55
Br-Benzene	155.5	1.70	1.95	3.59	3.81	2.81	6.50	6.56
I-Benzene	188.6	1.70	3.13	5.59	6.64	8.43	12.58	12.64
Cumene	151.5	0.65	1.98	3.74	4.48	2.81	7.34	10.62
p-Cymene	177.0	N.A.	2.68	3.80	6.25	2.80	8.00	a
o-Cl-Toluene	158.0	1.57	1.80	2.80	5.02	2.62	4.21	9.31
m-Cl-Toluene	161.0	N.A.	2.48	3.09	4.32	2.68	4.25	9.94
p-Cl-Toluene	167.0	2.21	2.19	2.24	4.29	2.81	4.28	9.95
o-Br-Toluene	181.8	N.A.	N.A.	N.A.	N.A.	2.70	4.16	9.34
m-Br-Toluene	183.7	N.A.	N.A.	N.A.	N.A.	2.73	4.19	9.64
p-Br-Toluene	184.0	N.A.	N.A.	N.A.	N.A.	2.77	4.23	9.74
m-DiCl-benzene	172.0	1.68	N.A.	N.A.	N.A.	1.07	2.62	5.62
o-DiCl-benzene	181.0	2.51	1.96	2.16	a	4.23	6.56	9.96

[a] All results are negative.
[b] a = Unable to calculate due to rounded peak tops and excessive tailing.
[c] N.A. = not available.

TABLE III

ADJUSTED RETENTION VOLUMES AND HEATS OF ADSORPTION FOR SELECTED AROMATIC COMPOUNDS ON BARIUM CHLORIDE AT 250°, 200°, 170°

Compound	*b.p.*(°C)	*Adjusted retention volume (ml)*			*Heat of adsorption (kcal/mole)*[a]
		250°C	*200°C*	*170°C*	
o-Toluidine	199.8	1.2	3.0	13.5	5.57
m-Toluidine	203.0	1.8	4.9	18.3	6.09
o-Cl Aniline	208.8	1.6	2.3	16.9	2.23
o-NO_2 Toluene	222.3	1.7	2.6	17.3	2.59
Nitrobenzene	210.9	4.6	8.0	30.2	3.37
o-Anisidine	225.0	3.4	8.6	31.0	6.83
m-Nitrotoluene	231.0	2.0	3.3	15.8	3.06

[a] All results are negative.

heats of adsorption on the barium halide columns seems to be a combined results of the increased electropositive character of the larger barium ion and the difference in polarity between methanol and ethanol. It also could be attributed to the solubility differences of the barium and strontium halides in methanol and ethanol. Anhydrous $SrCl_2$ is sparingly soluble in methanol, whereas $BaCl_2$ is moderately soluble. The bromide and iodide of barium and strontium are readily soluble in methanol[15].

Chain branching appears to have a significant effect on the heat of adsorption.

The data for the normal and branched alcohols support this observation. Increased branching usually results in an increase in the heat of adsorption. This increase in adsorption is partly due to the change in structure resulting from the increasing number of alkyl groups in the α- and β-positions to the hydroxyl group. These alkyl groups would effectively orient the hydroxyl group in reference to the solid surface seen by the molecule. This can be seen by comparison of the alcohol structures in Table IV.

Carboxylic acids

The heats of adsorption for the carboxylic acids increase as the boiling point increases and, as in the case of the alcohols, branching of the acids results in affecting the heat of adsorption. The absence of any anomalous results for formic and acetic acids, which might compare with the heat of adsorption for methanol and ethanol indicates the possibility of gas phase dimer formation. The carboxylic acids were eluted from strontium and barium iodide and barium bromide columns only under the most severe conditions. The resulting peaks were characterized by rounded tops and excessive tailing. Calculations of heats of adsorption for these samples were not possible.

Aromatic samples

The aromatic samples in Table II exhibit a variety of different interactions. As one adds electron releasing groups to the ring, the heat of adsorption increases. This increase also corresponds to the increase in boiling point, but appears unrelated to the change in gas phase dipole moment. The electron releasing methyl group in the series benzene, toluene, *m*-xylene, and mesitylene increases the π-electron density in the ring and consequently allows for successively greater adsorption.

Consideration of the halogenated benzenes, which have the same gas phase dipole moments, show that their heats of adsorption increase in a trend corresponding to their boiling points. They also follow the trend of charge transfer stabilities between Ag^+ with benzene and halobenzenes[16]. The halogen atom is an electron withdrawing group and decreases the electron density in the ring. As a result of this decrease in π-electron density the halobenzenes are not as strongly adsorbed as the alkyl substituted aromatics of comparable boiling point. A comparison of the heats of adsorption for cumene (b.p. 151.5°) and bromobenzene (b.p. 155.5°) on both the strontium and barium halide columns, and toluene (b.p. 110.6°) and chlorobenzene (b.p. 132.0°) on the strontium halide columns supports this observation. This data appears to be in good agreement with similar results published by ALTENEAU AND ROGERS[8] and BROOKMAN AND SAWYER[10]. Fig. 1 shows a plot of ΔH_a *versus* boiling point for the halobenzenes. With the exception of the barium bromide column there is a gradual increase in heat of adsorption progressing from benzene to chlorobenzene to bromobenzene. One then notes a big increase in ΔH_a from bromobenzene to iodobenzene. This same type of trend is noted with the relative charge transfer stabilities of the Ag^+ with the same four compounds[16].

Combining the electron withdrawing halogen and the electron releasing alkyl groups should yield a heat of adsorption somewhat lower than that obtained for a dialkyl substituted aromatic of comparable boiling point. This is found to be true when one considers the heat of adsorption for *p*-chlorotoluene (b.p. 162.4°) compared to *p*-xylene (b.p. 138.4°) on the strontium halide columns, and *p*-bromotoluene (b.p.

TABLE IV

EFFECT OF SUBSTITUENTS

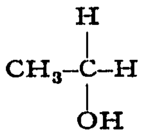
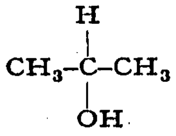
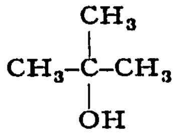
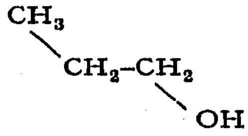
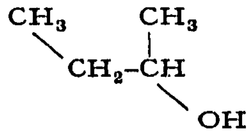
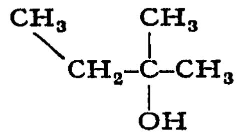
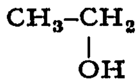
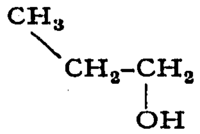
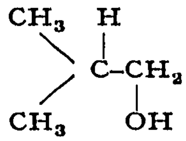
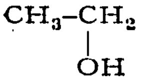
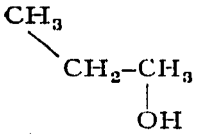
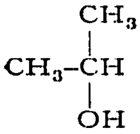
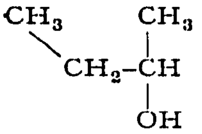
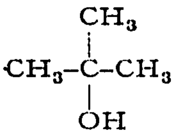
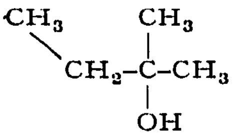
Compound	*Substituent*				$-\Delta H_a$		
	α	*β*	*b.p.*	*μ*	*$SrCl_2$*	*$SrBr_2$*	*SrI_2*
 $CH_3{-}\overset{H}{\underset{OH}{C}}{-}H$	—	—	78.5	1.71	1.51	3.69	8.59
 $CH_3{-}\overset{H}{\underset{OH}{C}}{-}CH_3$	1	—	82.0	1.59	1.21	1.26	4.67
 $CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3$	2	—	82.8	—	1.66	1.80	3.10
	—	1	97.0	1.66	1.27	1.37	4.98
	1	1	99.0	—	1.72	3.60	5.45
	2	1	102	—	1.95	3.63	5.49
 $\underset{OH}{CH_3{-}CH_2}$	—	—	78.5	1.71	1.51	3.69	8.59
	—	1	97.0	1.66	1.27	1.37	4.98
	—	2	108	1.64	1.79	2.86	7.52

TABLE IV (*continued*)

Compound	*Substituent*				$-\Delta H_a$		
	α	β	*b.p.*	μ	$SrCl_2$	$SrBr_2$	SrI_2
 $CH_3\text{-}\underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	—	—	78.5	1.71	1.51	3.69	8.59
	—	1	97.0	1.66	1.27	1.39	4.98
 $CH_3\text{-}\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle OH}{\underset{\vert}{CH}}}}$	1	—	82.0	1.59	1.21	1.26	4.67
	1	1	99.0	—	1.72	3.60	5.45
 $CH_3\text{-}\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle OH}{\underset{\vert}{C}}}}\text{-}CH_3$	2	—	82.8	—	1.66	1.80	3.10
	2	1	102.0	—	1.95	3.63	5.49

184°) compared to *p*-cymene (b.p. 177°) on the barium halide columns. The apparent deviation of *p*-chlorotoluene and *p*-xylene on barium chloride and iodide from the trend postulated above is possibly attributable to the increased ionic radius and electropositive character of the barium ion.

The dichlorobenzenes in Table II were studied briefly. The *ortho* isomer is adsorbed to a much greater extent than the *meta* isomer. This increase corresponds to both boiling point and gas phase dipole moment increase. The magnitude of the difference in heat of adsorption between the *ortho* and *meta* isomers, however, is surprising. It was earlier stated that the halogen withdraws electrons, decreases π-electron density and thus decreases adsorption. In the case of the *meta* isomer this explanation still appears valid. For the *ortho* isomer, it seems that the positioning of the electron withdrawing groups on two adjacent carbons increases the electron density in that region to such a great extent as to result in a significantly large increase in heat of adsorption over the *meta* isomer.

Fig. 2 illustrates the marked effect of going from chloride to iodide salts when utilizing the barium halides as packings. Very little separation occurs on the barium

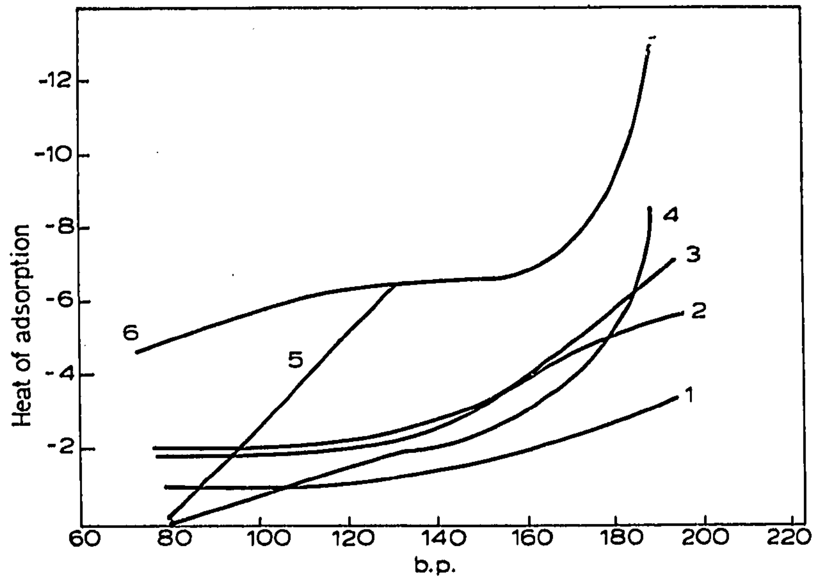


Fig. 1. Variation in ΔH_a *vs.* b.p. for halobenzenes. Boiling points: benzene, 80.0°; chlorobenzene 132.0°; bromobenzene 155.5°; iodobenzene 188.6°. Curve No.: 1 = $SrCl_2$ column; 2 = $SrBr_2$ column; 3 = SrI_2 column; 4 = $BaCl_2$ column; 5 = $BaBr_2$ column; 6 = BaI_2 column.

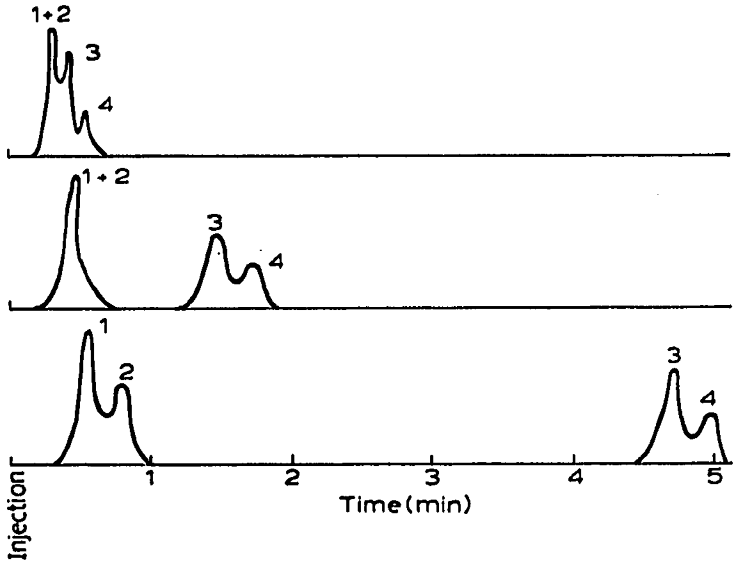


Fig. 2. Separation of various compounds on the barium halide columns. Conditions: temperature, 200°; flow rate, 60 ml/min; sample size, 1.0 µl. Compounds: 1 = hexane; 2 = bromocyclohexane; 3 = cumene; 4 = 1,2,4,-trichlorobenzene.

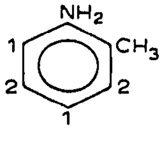
chloride column, whereas a separation of pairs occurs on the barium bromide column. However, a peak is obtained for each component on the barium iodide column.

Special aromatic samples (nitrogen substituted benzenes)

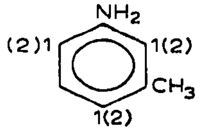
Due to the high boiling points of these isomers, a complete set of data was only obtained with the barium chloride column. All other columns produced peaks with rounded tops and excessive tailing.

The nitrogen substituted benzenes produced an interesting array of data. Table III listed the adjusted retention volumes and heats of adsorption for these compounds on the barium chloride column.

If one looks at the data for *o*- and *m*-toluidines, one can see that *m*-toluidine possesses a larger heat of adsorption and larger adjusted retention volume than those given for *o*-toluidine. This can probably be explained by an increase in boiling point and also by a greater increase in electron density. This increased electron density in *m*-toluidine may be explained by the structures below.



ortho



meta

(1) Refers to increased electron density due to NH_2
(2) Refers to increased electron density due to CH_3
From attempts to chemically substitute an aromatic ring system of this type, we know that substitution would predominate *ortho* and *para* to the strongest electron releasing group, *i.e.*, to the amino group. In the *ortho* isomer there is increased electron density in four unsubstituted ring positions. In this structure there are two areas of high electron density and two of less electron density. The *meta* isomer has three areas of extremely high electron density and one of low electron density. In the *meta* product, the two releasing groups supplement each other to produce areas of great density[9]. This should explain the increased adsorption of the *meta* product. The above explanation was based upon the fact that in *o*- and *m*-toluidine one has a strong activating amino group and a weakly activating methyl group. These groups donate electron density into the ring and are *ortho* and *para* directors.

It is also possible that steric effects cause a decrease in adjusted retention volumes and heats of adsorption for the *ortho* isomer because nitrogen's electrons may be partially blocked from the column packing whereas this condition should not arise in the *meta* isomer.

When the methyl group in *o*-toluidine is replaced with a chloride group, as in *o*-chloroaniline, the adjusted retention volumes and heats of adsorption decrease. This is expected since the chloride group is electron withdrawing.

If one now compares *o*-nitrotoluene to nitrobenzene, a decrease in adjusted retention volume and heat of adsorption is seen even though the boiling point has increased twelve degrees. Since the nitro group withdraws electrons from the ring, an activating group placed in the *ortho* position would decrease adsorption.

Looking at *o*-nitrotoluene and *m*-nitrotoluene, one sees an increase in adjusted retention volume and heats of adsorption. This is probably due to the nine degrees increase in boiling point and also to an increase in dipole moment from *o*- to *m*-nitrotoluene.

o-Anisidine has a higher heat of adsorption than that reported for *o*-toluidine. This may be due to a large boiling point increase and/or the presence of the weakly activating methyl group being replaced with a strong activating methoxy group. This increased electron donating effect should produce a larger heat of adsorption and an increase in adjusted retention volume.

It is also possible that an interaction between the electrons of nitrogen and oxygen (in NO_2) and the column packing cation were partially responsible for some of the above trends.

Some generalities can be drawn for the nitrogen substituted benzenes. Boiling point, in most cases, determines elution order. The heats of adsorption trends could have been produced by the sum of three effects: (1) interaction with the electrons of oxygen and nitrogen and the column packing, (2) interaction between the electrons of the aromatic nucleus and the cation, (3) increases in boiling point. It was noted that electron releasing groups enhance adsorption and electron withdrawing groups decrease adsorption.

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