

EVALUATION OF ALKALI METAL CHLORIDES AND NITRATES AS COLUMN PACKINGS IN GAS-SOLID CHROMATOGRAPHY

ROBERT L. GROB, GEORGE W. WEINERT* AND JOSEPH W. DRELICH

Chemistry Department, Villanova University, Villanova, Pa. (U.S.A.)

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INTRODUCTION

In October 1960, HANNEMAN, SPENCER AND JOHNSON¹ employed eutectic mixtures of lithium, sodium, and potassium nitrates in the temperature range from 150–400°. This work was in the realm of GLC. In a further study by HANNEMAN², an experimentally determined ΔH_a plot to 135° was a straight line for this eutectic mixture. This was 15° below the melting point of the eutectic mixture, hence, he was the first user of inorganic salts as adsorbents in gas chromatography.

FAVRE AND KALLENBACH³ began investigation of a number of inorganic salts (25%, by weight) adsorbed on Chromosorb P to separate *o*, *m* and *p*-terphenyls. They indicated little relationship existed between cation-anion changes and suggested adsorption was primarily dependent upon surface characteristics.

SOLOMON^{4,5} also studied *o*, *m* and *p*-terphenyls and a variety of other compounds displaying various polarities. He employed Chromosorb P as the support for inorganic salts. Generally, he observed that the more polar compounds eluted at a higher temperature than the less polar even though the boiling points may be the same. He studied alkali metal chlorides, sulfates, and carbonates. Much of his studies were devoted to lithium chloride. He found 0% LiCl on Chromosorb P, yielded excessive tailing and 100% indicated the opposite effect, *i.e.*, peaks rose gradually and fell sharply after the maximum was reached. Intermediate concentrations yielded sharp symmetrical peaks.

SOLOMON concluded that separation by solids is effected by (1) weak bonding between the inorganic salt and the organic molecules or (2) by a modification of the adsorption sites of the column support which then react with the organic molecule.

Some generalizations from his studies are:

(a) Melting point of the solid has little effect upon column performance.

(b) If two salts are mixed retention properties are the average of the two when adjusted for concentration.

(c) Anion-cation effects are significant. For example, sulfates cause elution temperatures to increase when compared to chlorides.

ROGERS AND ALTENAU⁶⁻⁸ discovered that certain inorganic complexes display a wide variety of adsorptive characteristics. Water, pyridine, or ammonia were pyrolytically eliminated to produce very porous solids with relatively large surface

* Geigy Chemical Company, Cranston, R.I. (U.S.A.).

areas when compared to the starting materials. Organic solutes displaying various polarities were studied. These studies showed oxygenated compounds were held most strongly and aliphatic compounds least strongly. Amines with a lone pair of electrons do not desorb. They postulated interaction occurs between the metal in the complex and either the lone pair or pairs of electrons in nitrogen or oxygen or with the π electron system in aromatic compounds, and lastly by induced dipoles in the aliphatic series.

This paper deals with a logical evaluation of both the alkali chlorides and alkali nitrates employing non-polar, polar, and aromatic compounds.

EXPERIMENTAL

Reagents

Salts. The following salts were acquired from J. T. Baker Chemical Company (Phillipsburg, N.J.) and were "Baker Analyzed" quality: LiCl, NaCl, KCl, LiNO₃, NaNO₃, and KNO₃. Matheson, Coleman, and Bell (East Rutherford, N.J.) supplied RbCl. K and K Laboratories (Plainfield, N.Y.) supplied CsCl, RbNO₃, and CsNO₃.

Solutes. J. T. Baker Chemical Company (Phillipsburgh, N.J.) supplied *m*-hexame, isopropanol, *n*-amyl alcohol, and isoamyl alcohol. Fisher Scientific Company (Fair Lawn, N.J.) supplied *n*-pentane, *n*-propamol, *m*-butamol, isobutamol, and *tert*-amyl alcohol. K and K Laboratories (Plainfield, N.Y.) supplied 2,2-dimethylpropamol. Matheson, Coleman, and Bell (East Rutherford, N.J.) supplied 3-methylpentane, 2,2-dimethylbutane, and 2-methylpentanol, as well as high purity methane, ethane, propane, butane, and isobutane in lecture bottles. Eastman Organic Chemicals (Rochester, N.Y.) supplied 2-methylbutane, *sec*-butamol, and *m*-hexamol. Chem. Service, Inc. (Media, Pa.) supplied all remaining chemicals.

Apparatus

Instruments. The instrument employed was a Perkin-Elmer Model 154-D Vapor Fractometer manufactured by the Perkin-Elmer Corp. (Norwalk, Conn.). A Leeds and Northrup Speedomax Model H Recorder, with a 1 mV chart span, manufactured by the Leeds and Northrup Company, Philadelphia, Pa., was used throughout this investigation.

Accessories. Hamilton syringes were employed for all liquid samples. Gas sampling was effected through the use of the gas sampling valve in the instrument.

A soap bubble flow meter was constructed from a 10.0 ml burette.

Column preparation. The alkali metal salts were ground by means of a mortar and pestle and then sieved to 60-80 mesh size. Copper tubing (O.D. 0.25 in., I.D. 0.23 in.) was cut to 320 cm and cleaned with acetone and helium gas to remove any grease and/or dust particles. The LiCl column was prepared in a dry nitrogen atmosphere because of its very deliquescent nature. The column packing was added and the column was vibrated to ensure dense packing. Quarter-inch plugs of glass wool were used in both ends of the tubing. The columns were then preconditioned for a minimum of 2 h at 200° with a helium flow rate of 100 cc/min. CsCl, RbNO₃, and LiNO₃ were preconditioned for only 2 h; all other columns were preconditioned for 24 h. In all cases the criterion for ending conditioning was the base-line stability. Although the base line was stable for all columns after one hour of operation; it was decided that it

would be wise to add at least an additional hour to ensure removal of all volatile contaminants.

Sampling procedure

It was discovered that the frequency of injection effected the retention characteristics of some of the higher boiling compounds studied. It was also noticed that the first injection of a sample had a slightly larger retention time; the magnitude was in the order of 0.1 sec. Thus, it was decided to standardize the sampling procedure. Each sample was injected with exactly 1 min between successive injections. When the retention time was close to a 1 min (within 10 sec) interval, 2 min elapsed between injections. This same procedure was employed for the air samples.

The adsorbent properties of the alkali salts were studied using one microliter samples. The data presented was the result of five repetitive sample injections. This number of sample injections was justified after the precision shown in Table I was determined.

Gas sampling was done in an analogous (1 min intervals) manner. The flow rate of the gas samples through the gas sample valve were difficult to control; all were essentially 60 cc/min (± 10 cc/min). All retention volumes are numerically equal to

TABLE I

PRECISION DETERMINATION (BENZYLAMINE)

Conditions: column KCl, 60-80 mesh; temperature, $121^\circ \pm 1.0^\circ$; flow rate, 60 cc/min; retention time of air (ten repetitive samplings), 35.7 sec.

*Retention time for
benzylamine (sec)*

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42.3
42.2
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42.3
42.3
42.4
42.3

4229.0

\bar{X} = 42.3 = mean

d = 0.02 = average deviation of a single measurement

s = 0.0284 = standard deviation of a single measurement

\bar{s} \times 0.064 = standard deviation of the mean

TABLE II

ADJUSTED RETENTION VOLUMES (V_R') ON ALKALI METAL CHLORIDE COLUMNSConditions: flow rate (60 cc/min); sample size 1 μ l.

	B.p.	V_R'				
		LiCl (3x ²)	NaCl (3x ²)	KCl (3x ²)	RbCl (3x ²)	CsCl (3x ²)
<i>A. Alkanes</i>						
Methane	-16.1	a	a	a	a	a
Ethane	-88	a	a	a	a	a
Propane	-42	a	a	a	a	a
Butane	-50	0.1	a	a	0.2	a
Isobutane	-11	a	a	a	0.1	a
n-Pentane	36	0.7	0.3	0.2	0.6	0.3
2,2-Dimethylpropane	9	0.1	a	a	0.4	a
2-Methylbutane	27	0.6	0.1	a	0.5	0.2
n-Hexane	69	2.7	2.2	2.1	3.1	1.7
3-Methylpentane	63	2.2	1.9	1.7	2.6	1.3
2-Methylpentane	60	1.9	1.5	1.4	2.2	1.2
2,2-Dimethylbutane	50	1.3	0.9	0.8	1.5	0.7
2,3-Dimethylbutane	58	1.8	1.5	1.2	2.1	1.0
	B.p.	V_R'				
		LiCl (12x ²)	NaCl (12x ²)	KCl (12x ²)	RbCl (12x ²)	CsCl (12x ²)
<i>B. Alcohols</i>						
Methanol	64.7	0.2	b	0.2	b	b
Ethanol	78.4	0.1	b	0.1	b	b
n-Propanol	97.2	0.7	b	0.5	1.2	b
Isopropanol	82.4	0.2	b	0.2	0.3	b
n-Butanol	118.0	1.3	2.1	1.2	1.5	0.9
Isobutanol	108.1	1.0	1.3	0.8	0.7	0.5
sec.-Butanol	99.5	0.6	0.7	0.6	1.1	0.3
tert.-Butanol	82.6	a	0.2	0.2	0.2	a
n-Amyl alcohol	138.0	2.6	4.5	2.6	3.4	1.9
Isoamyl alcohol	132.0	2.0	3.3	2.0	2.7	1.5
2,2-Dimethylpropanol	c	b	8.7	b	b	b
3-Pentanol	116.0	0.7	1.1	1.0	1.1	0.5
2-Methyl-2-butanol	102.4	0.4	0.7	0.7	0.7	0.3
n-Hexanol	157.5	5.0	7.1	5.4	7.1	3.8
2-Hexanol	139.0	2.1	3.1	2.7	3.3	2.7
3-Hexanol	135.0	0.6	3.3	2.1	2.7	1.2
4-Methylpentanol	151.0	3.8	6.1	4.7	5.6	3.1
3-Methylpentanol	152.0	2.3	6.2	3.4	5.4	3.2
2-Methylpentanol	148.0	3.8	6.1	4.7	5.6	3.1
2-Methyl-2-pentanol	122.5	1.0	1.8	1.4	1.6	0.8
2-Methyl-3-pentanol	127.5	1.2	1.9	1.3	1.8	1.0
3-Methyl-3-pentanol	122.0	1.0	1.8	1.4	1.6	0.8
3-Methyl-4-pentanol	137.0	1.7	b	2.1	2.5	1.3
4-Methyl-2-pentanol	131.8	1.4	2.2	1.7	2.0	1.0
<i>C. Other samples</i>						
2,3,4-Trimethylpentane		a	a	a	a	a
n-Nonane	150.0	0.3	0.4	a	a	a
n-Octyl alcohol	195.0	9.9	9.2	6.3	8.8	b

* a == V_R' equal to zero; b == not evaluated under these conditions; c == 20% in acetone.

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TABLE II (continued)

	<i>B.p.</i>	<i>V_R'</i> **				
		<i>LiCl</i> (120°)	<i>NaCl</i> (120°)	<i>KCl</i> (120°)	<i>RbCl</i> (120°)	<i>CsCl</i> (120°)
<i>n</i> -Decane	174.0	1.4	1.2	a	a	a
2,2,5-Trimethylhexane		a	a	a	0.1	a
Butylamine	77.0	0.8	0.7	0.1	0.1	a
<i>sec.</i> -Butylamine	63.0	0.4	0.7	a	a	a
Isobutylamine	69.0	0.4	0.2	a	a	a
<i>tert.</i> -Butylamine	46.0	a	a	a	a	a
Aniline	184.0	8.2	7.2	5.1	5.6	b
Benzylamine	185.0	13.2	10.6	6.6	6.3	b
2,4-Dimethylaniline	244.0	21.8	21.8	16.1	16.1	b
<i>o</i> -Toluidine	199.0	12.1	12.3	9.8	9.5	b
<i>m</i> -Toluidine	203.0	15.0	13.2	10.9	10.6	b
<i>o</i> -Anisidine	225.0	30.0	25.0	23.8	23.6	b
<i>o</i> -Chloroaniline	208.0	12.3	13.9	13.3	13.0	b
<i>m</i> -Chloroaniline	229.0	23.8	30.3	27.7	28.5	b
<i>m</i> -Chlorotoluene	162.0	1.2	1.5	1.4	1.9	a
<i>p</i> -Chlorotoluene	162.0	1.2	1.3	1.5	1.9	a
2-Picoline	128.0	1.0	0.3	0.4	0.7	a
3-Picoline	143.0	2.3	1.5	1.3	1.3	a
4-Picoline	143.0	1.6	1.6	1.5	1.4	a
Benzene	80.0	a	a	a	a	a
2-Heptanone	150.0	0.7	0.9	0.8	1.1	a
3-Heptanone	148.0	0.5	0.6	a	0.3	1.0
<i>m</i> -Cresol	202.8	11.9	15.1	13.3	17.4	b
<i>p</i> -Cresol	202.5	12.1	15.5	13.8	18.2	a
<i>o</i> -Xylene	144.4	0.4	0.2	a	0.5	0.9
<i>m</i> -Xylene	139.0	0.2	0.1	0.3	0.6	a
<i>p</i> -Xylene	138.0	0.2	0.1	a	0.1	0.7
Nitrobenzene	210.0	9.6	15.6	15.1	14.4	b
1-Nitropropane	132.0	0.1	0.3	0.3	0.7	b
2-Nitropropane	120.0	a	0.2	a	0.5	a
Pyridine	153.3	1.7	0.5	0.3	0.6	a

the retention time, in sec, *i.e.*, the flow rate, in all cases, was 60 cc/min. All retention volumes are adjusted to air, *i.e.*

$$V_R' = V_R - V_M(\text{air})$$

DATA AND DISCUSSION

Retention volumes for the various compounds studied are found in Tables II and III. Heats of adsorption for these compounds on the alkali salt columns are found in Tables IV and V.

Retention volume is discussed extensively for the nitrate columns and heats of adsorption extensively for the chloride columns. The principles are valid in both cases; we decided not to repeat ourselves.

I. Retention volume

1. Chloride columns

Representative data are found in Table II.

TABLE III

ADJUSTED RETENTION VOLUMES (V_R') ON ALKALI METAL NITRATE COLUMNSConditions: flow rate 60 cc/min; sample size 1 μ l.

	<i>B.p.</i>	$V_R'^*$				
		$LiNO_3$ (30°)	$NaNO_3$ (30°)	KNO_3 (30°)	$RbNO_3$ (30°)	$CsNO_3$ (30°)
<i>A. Alkanes</i>						
Methane	-161.5	a	a	a	a	a
Ethane	- 88.3	a	a	a	a	a
Propane	- 42.17	a	a	a	a	a
<i>n</i> -Butane	0.5	a	a	a	a	a
Isobutane	- 12.0	a	a	a	a	a
<i>n</i> -Pentane	36.1	0.7	0.8	0.6	1.5	1.7
2,2-Dimethylpropane	9.5	0.1	a	a	0.3	a
2-Methylbutane	28.0	0.4	0.6	0.4	1.0	1.3
<i>n</i> -Hexane	68.7	3.4	3.0	3.0	5.5	6.3
3-Methylpentane	63.3	2.7	2.4	2.5	4.6	5.4
2-Methylpentane	60.3	2.4	2.1	2.1	4.1	4.5
2,2-Dimethylbutane	49.7	1.4	1.5	1.4	2.9	3.4
2,3-Dimethylbutane	58.0	2.0	2.0	1.9	3.9	4.4
	<i>B.p.</i>	$V_R'^*$				
		$LiNO_3$ (120°)	$NaNO_3$ (120°)	KNO_3 (120°)	$RbNO_3$ (120°)	$CsNO_3$ (120°)
<i>B. Alcohols</i>						
Methanol	64.7	0.2	0.5	a	0.3	0.2
Ethanol	78.3	a	0.7	a	0.2	0.2
<i>n</i> -Propanol	97.2	0.5	2.0	a	0.9	1.1
Isopropanol	82.3	0.1	0.9	a	0.3	0.4
<i>n</i> -Butanol	117.7	1.2	3.7	a	1.3	2.2
<i>sec.</i> -Butanol	99.5	0.4	1.9	a	1.1	1.2
Isobutanol	107.9	0.8	2.7	a	1.7	1.7
<i>tert.</i> -Butanol	82.5	a	0.9	a	0.4	0.3
<i>n</i> -Amyl alcohol	138.0	2.6	8.8	3.6	5.0	4.4
Isoamyl alcohol	131.5	2.0	6.3	2.6	4.0	3.6
<i>tert.</i> -Amyl alcohol	101.8	0.5	2.0	0.9	1.5	1.6
2,2-Dimethylpropanol in acetone	113.0	a	12.1	a	8.3	1.9
3-Pentanol	116.1	0.9	2.6	1.5	2.1	2.5
2-Methyl-2-butanol	102.4	0.4	1.9	0.7	1.2	a
<i>n</i> -Hexanol	157.5	5.4	17.9	6.3	9.9	8.7
2-Hexanol	139.0	2.4	5.4	3.2	5.2	5.3
3-Hexanol	135.0	1.9	3.6	2.6	3.9	4.8
4-Methylpentanol	151.0	4.2	13.1	5.1	7.9	7.1
3-Methylpentanol	152.0	4.1	12.1	5.0	8.1	9.2
2-Methylpentanol	148.0	3.4	10.1	4.2	6.7	7.6
2-Methyl-2-pentanol	122.5	1.1	2.2	1.4	2.8	3.1
2-Methyl-3-pentanol	127.5	1.5	2.5	1.7	3.0	3.2
3-Methyl-3-pentanol	122.0	1.2	2.9	1.5	2.7	2.4
3-Methyl-4-pentanol	137.0	1.9	3.6	2.5	4.2	3.6
4-Methyl-2-pentanol	131.8	1.7	3.6	2.1	3.7	3.8

* a = V_R' equal to zero.

(continued on p. 311)

TABLE III (continued)

	B.p.	V_R^*				
		$LiNO_3$ (120°)	$NaNO_3$ (120°)	KNO_3 (120°)	$RbNO_3$ (113°)	$CsNO_3$ (115°)
<i>C. Other samples</i>						
2,3,4-Trimethylpentane		a	a	a	0.3	0.3
<i>n</i> -Nonane	150.7	0.4	0.6	0.4	1.2	0.8
<i>n</i> -Octyl alcohol	195.0	8.8	8.0	6.5	16.2	14.7
<i>n</i> -Decane	174.0	1.4	1.9	1.2	3.1	2.5
2,2,5-Trimethylhexane		a	0.3	a	0.6	0.6
Butylamine	77.8	0.3	0.8	a	0.3	a
<i>sec.</i> -Butylamine	63.0	a	0.5	a	a	a
Isobutylamine	68.9	a	0.7	a	a	a
<i>tert.</i> -Butylamine	46.6	a	0.5	a	a	a
Aniline	184.0	6.9	5.4	5.6	10.2	8.3
Benzylamine	185.0	14.7	7.4	5.7	10.4	8.5
2,4-Dimethylaniline	244.0	19.3	16.5	15.7	26.4	22.2
<i>o</i> -Toluidine	199.0	11.8	9.4	9.4	15.5	12.7
<i>m</i> -Toluidine	203.0	13.8	10.5	12.5	18.4	15.6
<i>o</i> -Anisidine	225.0	30.2	22.6	25.3	36.8	31.7
<i>o</i> -Chloroaniline	208.0	15.7	12.9	13.0	20.4	17.6
<i>m</i> -Chloroaniline	229.0	35.1	26.7	28.3	42.2	35.7
<i>m</i> -Chlorotoluene	162.0	1.9	2.0	1.5	3.1	2.6
<i>p</i> -Chlorotoluene	162.0	1.9	2.1	1.5	3.2	2.6
2-Picoline	128.0	1.0	0.9	0.4	1.4	1.1
3-Picoline	143.0	2.8	1.9	1.2	2.8	2.1
4-Picoline	143.0	3.6	2.3	1.3	3.0	2.4
Benzene	80.0	a	a	a	a	a
2-Heptanone	150.0	1.1	1.7	0.8	2.5	1.8
3-Heptanone	148.0	0.9	1.4	0.7	1.9	1.5
<i>m</i> -Cresol	202.8	15.9	13.5	14.4	23.0	19.2
<i>p</i> -Cresol	202.5	16.4	18.4	14.0	23.4	19.1
<i>o</i> -Xylene	144.4	0.8	0.9	0.5	1.4	1.3
<i>m</i> -Xylene	139.0	0.5	0.7	0.3	1.3	1.0
<i>p</i> -Xylene	138.0	0.5	0.7	0.3	1.2	1.1
Nitrobenzene	210.0	15.7	14.3	13.7	21.3	17.7
1-Nitropropane	132.0	0.5	0.9	0.3	1.3	0.9
2-Nitropropane	120.0	0.3	0.6	a	0.8	0.6
Pyridine	153.3	1.1	1.0	0.3	1.2	0.8

2. Nitrate columns

A. Alkanes

We have a complete set of data only for the hexanes. All other alkanes investigated either eluted with air or some of the isomers in a group of compounds eluted with air. We will consider only a complete set of data. Retention volumes are found in Table III.

n-Hexane has the greatest retention volume on all columns at all temperatures. If we had a synthetic mixture of the five hexane isomers we would expect elution order to be determined by the boiling points of the compounds. That order would be *n*-hexane, 3-methylpentane, 2-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

The elution order on all columns under all conditions is precisely this order (an

TABLE IV

HEATS OF ADSORPTION ON ALKALI METAL CHLORIDE COLUMNS

Conditions: temperature 50°, 40°, 30°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*				
	LiCl	NaCl	KCl	RbCl	CsCl
<i>A. Alkanes</i>					
<i>n</i> -Hexane	6.71	12.10	8.42	8.22	10.35
3-Methylpentane	5.82	12.70	10.35	8.14	5.21
2-Methylpentane	5.06	14.50	6.88	8.02	5.73
2,2-Dimethylbutane	6.09	16.50	2.75	7.21	3.07
2,3-Dimethylbutane	5.57	14.50	9.10	8.03	2.11

Conditions: temperature 180°, 150°, 120°, 105°, 90°, 70°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*				
	LiCl	NaCl	KCl	RbCl	CsCl
<i>B. Alcohols</i>					
Methanol	21.52	13.40	8.62	13.25	n.a.
Ethanol	17.21	2.60	14.17	10.41	n.a.
<i>n</i> -Propanol	7.34	10.49	9.80	8.61	n.a.
Isopropanol	5.56	14.80	11.14	9.92	16.54
<i>n</i> -Butanol	8.43	9.88	12.99	9.30	10.88
<i>sec.</i> -Butanol	7.02	6.54	15.39	9.49	13.92
<i>tert.</i> -Butanol	9.84	23.11	14.89	15.45	n.a.
<i>n</i> -Amyl alcohol	6.47	13.20	12.21	11.34	10.97
Isoamyl alcohol	6.71	14.50	12.21	8.21	9.72
<i>tert.</i> -Amyl alcohol	n.a.	7.65	n.a.	11.74	15.12
2,2-Dimethylpropanol in acetone	9.46	10.90	12.85	9.54	13.23
3-Pentanol	17.71	3.42	14.79	9.92	12.96
2-Methyl-2-butanol	10.37	n.a.	18.19	13.06	n.a.
<i>n</i> -Hexanol	7.98	11.80	12.04	9.45	11.52
2-Hexanol	7.48	10.98	11.56	9.16	9.74
3-Hexanol	23.63	14.44	11.86	8.61	10.71
4-Methylpentanol	9.63	11.53	9.23	9.87	9.92
3-Methylpentanol	15.03	10.98	11.29	8.61	9.73
2-Methylpentanol	6.90	12.07	12.54	9.36	10.84
2-Methyl-2-pentanol	8.78	0.63	12.54	9.64	9.54
2-Methyl-3-pentanol	7.61	1.23	9.37	18.19	10.22
4-Methyl-2-pentanol	7.48	12.00	11.30	8.63	10.22
3-Methyl-3-pentanol	6.71	13.21	11.63	10.63	9.93
3-Methyl-4-pentanol	2.07	10.44	11.32	9.74	9.69
Isobutanol	5.57	n.a.	11.86	8.44	12.96
<i>C. Other samples</i>					
<i>n</i> -Octyl alcohol	22.42	16.06	13.25	9.87	n.a.
Butylamine	1.30	9.36	n.a.	n.a.	n.a.
<i>sec.</i> -Butylamine	0.10	5.64	n.a.	n.a.	n.a.
Isobutylamine	7.61	4.42	n.a.	n.a.	n.a.
Aniline	16.16	13.09	12.13	13.16	n.a.
Benzylamine	3.52	12.88	13.18	13.07	n.a.
2,4-Dimethylaniline	14.43	15.41	14.07	14.03	n.a.
<i>o</i> -Toluidine	17.32	14.20	13.85	13.49	n.a.

* All values negative; n.a. = not available.

(continued on p. 313)

TABLE IV (continued)

Conditions: temperature 180°, 150°, 120°, 105°, 90°, 70°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*				
	<i>LiCl</i>	<i>NaCl</i>	<i>KCl</i>	<i>RbCl</i>	<i>CsCl</i>
<i>m</i> -Toluidine	15.45	15.46	13.53	13.23	n.a.
<i>o</i> -Anisidine	16.23	13.29	14.16	14.58	n.a.
<i>o</i> -Chloroaniline	16.74	11.97	12.99	13.01	n.a.
<i>m</i> -Chloroaniline	13.05	12.81	13.04	14.31	n.a.
<i>m</i> -Chlorotoluene	10.12	n.a.	17.61	17.19	n.a.
<i>p</i> -Chlorotoluene	10.55	n.a.	22.20	17.19	n.a.
2-Picoline	25.42	5.64	n.a.	7.60	n.a.
3-Picoline	16.66	5.65	17.66	13.83	n.a.
4-Picoline	15.31	6.36	17.77	17.01	n.a.
2-Heptanone	n.a.	1.30	n.a.	14.35	n.a.
<i>m</i> -Cresol	17.23	13.61	15.06	15.18	n.a.
<i>p</i> -Cresol	17.41	12.71	15.15	14.72	n.a.
Nitrobenzene	12.13	12.74	14.39	13.34	n.a.
Pyridine	9.80	2.47	12.13	n.a.	n.a.

error of ± 0.1 cc, in retention volume, is considered within the realm of experimental error).

If we next consider all the values of a specific compound on all of the columns in order of decreasing retention volume, we have $\text{CsNO}_3 > \text{RbNO}_3 > \text{LiNO}_3 > \text{KNO}_3 = \text{NaNO}_3$. The most valid place to discover this trend appears to be at the lowest temperatures (30°). At higher temperatures the differences become smaller and any trends discovered are more liable to be in error.

This trend in elution order appears to exist for all of the hexanes. We emphasize that this appears to be true because this trend does exist for *n*-hexane and 3-methylpentane, which are the higher boiling compounds. The lower boiling compounds appear to follow when we consider a possible error of ± 0.1 cc, in retention volume.

B. Alcohols

All retention values are found in Table III. Some of the compounds found in this table are reproduced below in Table VI. Values given in this table are for the lowest temperature of evaluation. The alcohols are listed in increasing order of boiling points.

Chain branching appears to have a marked effect upon elution order. Specifically, *n*-propanol and *sec.*-butanol have approximately the same boiling point yet *n*-propanol is adsorbed more strongly. This is possibly due to a blocking effect of the hydroxy group, *i.e.*, the formation of alcoholate complexes; the ΔH_f of which are sensitive to the stereochemistry of the alcohol. From this data it appears that interaction is between the column packing and the electronegative portion of the sample molecule.

Table VII illustrates this effect more drastically with *n*-amyl alcohol and 3-methyl-4-pentanol.

Some generalities can be drawn from the data regarding the alcohols. The boiling point primarily determines elution order, however, when chain branching occurs, the more highly branched species elutes before the straight chain alcohol with identical

TABLE V

HEATS OF ADSORPTION ON ALKALI METAL NITRATE COLUMNS

Conditions: temperature 30°, 40°, 50°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*					ΔH_v kcal/ mole	Temp. (°C)
	LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃		
<i>A. Alkanes</i>							
Methane	n.a.	n.a.	n.a.	n.a.	n.a.	2.00	-176
Ethane	n.a.	n.a.	n.a.	n.a.	n.a.	3.60	96.7
Propane	n.a.	n.a.	n.a.	n.a.	n.a.	4.62	- 46.9
<i>n</i> -Butane	n.a.	n.a.	n.a.	n.a.	n.a.	5.47	- 1.8
Isobutane	n.a.	n.a.	n.a.	n.a.	n.a.	5.12	- 13.9
<i>n</i> -Pentane	n.a.	20.66	n.a.	10.39	9.86	6.12	38.9
2,2-Dimethylpropane	n.a.	n.a.	n.a.	n.a.	n.a.	5.44	9.1
2-Methylbutane	n.a.	18.03	n.a.	15.19	11.15	5.84	29.1
<i>n</i> -Hexane	10.35	9.10	11.08	7.46	8.02	6.92	74.8
3-Methylpentane	12.09	9.75	11.28	8.38	8.49	6.63	68.8
2-Methylpentane	9.75	10.91	10.66	7.29	8.12	6.56	65.4
2,2-Dimethylbutane	12.44	10.91	11.37	8.35	8.39	6.23	53.9
2,3-Dimethylbutane	10.44	11.96	11.03	7.86	7.46	6.44	62.9

Conditions: temperature 150°, 140°, 135°, 120°, 115°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*					ΔH_v kcal/ mole	Temp. (°C)
	LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃		
<i>B. Alcohols</i>							
Methanol	11.44	8.61	14.27	18.19	14.49	8.3	64
Ethanol	14.52	7.99	11.78	16.86	17.54	9.4	78
<i>n</i> -Propanol	9.09	9.00	8.64	11.18	10.46	9.8	97
Isopropanol	14.83	7.79	10.60	15.12	13.59	9.5	82
<i>n</i> -Butanol	7.75	13.95	7.85	14.95	8.19	10.5	116
<i>sec.</i> -Butanol	10.37	7.19	8.67	9.92	7.65	10.0	98
Isobutanol	8.37	10.81	8.40	9.19	9.93	10.2	106
<i>tert.</i> -Butanol	17.93	5.46	10.60	5.61	11.52	9.7	83
<i>n</i> -Amyl alcohol	6.34	13.09	9.56	11.16	12.69	10.6	131
Isoamyl alcohol	9.61	13.26	7.43	11.20	11.07	10.6	130
<i>tert.</i> -Amyl alcohol	9.10	7.65	6.89	11.54	15.89		
3-Pentanol	10.74	6.83	11.45	10.21	11.20		
2-Methyl-2-butanol	10.94	1.08	9.39	11.85	4.16		
<i>n</i> -Hexanol	10.59	14.24	10.99	10.91	12.15		
2-Hexanol	11.60	10.15	8.97	10.95	13.11		
3-Hexanol	12.10	7.04	9.29	10.20	12.07		
4-Methylpentanol	10.62	5.77	8.55	11.05	14.75		
3-Methylpentanol	10.83	11.14	8.44	10.90	10.74		
2-Methylpentanol	11.54	13.92	9.50	11.10	13.93		
2-Methyl-2-pentanol	15.94	14.55	6.96	8.71	15.94		
2-Methyl-3-pentanol	15.05	17.51	9.04	9.93	15.31		
3-Methyl-3-pentanol	16.31	7.07	9.04	9.06	14.32		
3-Methyl-4-pentanol	12.10	7.14	9.28	9.25	12.55		
4-Methyl-2-pentanol	12.23	7.14	9.14	9.77	11.85		
2,2-Dimethylpropanol	19.47	16.27	10.93	7.81	20.21		

* All values negative; n.a. = not available.

(continued on p. 315)

TABLE V (continued)

Conditions: temperature 150°, 140°, 135°, 120°, 115°; flow rate 60 cc/min; sample size 1 μ l.

	ΔH_a^*					ΔH_v kcal/ mole	Temp. (°C)
	LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃		
<i>C. Other samples</i>							
2-Picoline	n.a.	16.55	n.a.	23.83	n.a.		
3-Picoline	16.21	11.01	n.a.	15.56	n.a.		
4-Picoline	16.21	11.65	16.19	14.54	11.13		
Benzene	n.a.	n.a.	n.a.	n.a.	n.a.		
2-Heptanone	n.a.	14.84	n.a.	n.a.	11.57		
3-Heptanone	n.a.	11.37	n.a.	n.a.	18.16		
<i>m</i> -Cresol	15.02	13.14	14.70	13.43	10.51	11.32	202
<i>p</i> -Cresol	14.86	15.47	14.10	12.76	10.61	11.32	201.9
<i>o</i> -Xylene	n.a.	16.55	n.a.	n.a.	13.25	8.80	144
<i>m</i> -Xylene	n.a.	21.48	n.a.	n.a.	14.50	8.72	139
Nitrobenzene	14.10	13.36	12.29	13.27	11.79	10.36	210
1-Nitropropane	n.a.	18.86	n.a.	n.a.	n.a.		
2-Nitropropane	n.a.	19.78	n.a.	n.a.	n.a.		
Pyridine	n.a.	13.29	n.a.	n.a.	12.48	8.49	114
<i>n</i> -Octyl alcohol	16.21	13.28	11.96	13.34	n.a.		
Butylamine	n.a.	22.95	n.a.	n.a.	n.a.		
Isobutylamine	n.a.	21.48	n.a.	n.a.	n.a.		
Aniline	13.91	12.12	13.83	14.28	11.36	10.32	184
Benzylamine	14.65	10.34	12.13	14.11	n.a.		
2,4-Dimethylaniline	14.89	13.86	13.55	13.23	n.a.		
<i>o</i> -Toluidine	14.45	13.37	13.69	18.50	11.17	10.68	200.2
<i>m</i> -Toluidine	14.48	12.34	14.70	12.92	n.a.	10.72	203.4
<i>o</i> -Anisidine	14.68	13.58	13.27	13.87	12.46		
<i>o</i> -Chloroaniline	14.10	13.21	12.74	12.88	11.54	10.65	208
<i>m</i> -Chloroaniline	14.00	13.03	12.29	12.65	14.14	10.95	229
<i>m</i> -Chlorotoluene	21.57	17.76	17.77	18.49	n.a.		
<i>p</i> -Chlorotoluene	21.83	18.31	17.77	18.78	n.a.		

TABLE VI

RETENTION VOLUMES OF SOME ALCOHOLS ON ALKALI METAL NITRATE COLUMNS

Conditions: Temperature 90°; flow rate 60 cc/min; sample size 1.00 μ l.

	<i>B.p.</i>	V_R'				
		LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃
Methanol	64.7	0.8	1.7	0.7	0.9	1.0
Ethanol	78.3	0.6	2.0	0.6	1.3	1.4
Isopropanol	82.3	0.6	2.4	0.7	1.6	1.8
<i>tert.</i> -Butanol	82.5	0.6	1.8	0.7	1.7	2.0
<i>n</i> -Propanol	97.2	1.5	4.9	1.7	3.1	3.5
<i>sec.</i> -Butanol	99.5	1.4	3.4	1.6	3.3	2.8
Isobutanol	107.9	2.2	6.3	2.4	4.7	5.1
<i>n</i> -Butanol	117.7	3.6	9.2	3.6	6.8	5.8

boiling point. This appears to be governed by the availability of the polar hydroxy group to interact with the column.

TABLE VII

RETENTION VOLUMES OF A STRAIGHT CHAIN AND A BRANCHED CHAIN ALCOHOL WITH SIMILAR BOILING POINTS

Temperature: 120°.

	B.p.	V_R'				
		$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
<i>n</i> -Amyl alcohol	138.0	2.6	8.8	3.6	5.0	4.4
3-Methyl-4-pentanol	137.0	1.9	3.6	2.5	4.2	3.6

C. Other sample types

Table III lists the retention volumes of the special samples (referred to as such because they did not fit into the homologous series of the hydrocarbons and alcohols). A quick appraisal of the table indicates that boiling point generally determines the retention volume of the compounds. However, if we contrast the retention volumes of two compounds with equal boiling points on the same column at the same low temperature it appears that the polar character of a compound influences its elution. For example, we can contrast *n*-nonane and 2-heptanone on the rubidium nitrate and cesium nitrate columns at 113° and 115°, respectively. This data is presented in Table VIII.

TABLE VIII

RETENTION VOLUMES OF TWO COMPOUNDS WITH EQUAL BOILING POINTS

	B.p.	V_R'	
		$RbNO_3$ (113°)	$CsNO_3$ (115°)
<i>n</i> -Nonane	150.7	1.2	0.8
2-Heptanone	150.0	2.5	1.8

Apparently there is some interaction between the column and the oxygen of the ketone.

The remaining aromatic compounds can be classified with regard to derivative type. Let us consider three groups; benzene type derivatives, aniline type derivatives (which are benzene type but will be considered separately), and pyridine type compounds.

(i) *Benzene type compounds.* Table IX lists these compounds in order of increasing boiling point. Retention volumes are given in milliliters. Generally, higher boiling compounds elute after the lower boiling ones, yet other effects are seen. Benzene may have some interaction with the columns, but it is not displayed under these conditions. The xylenes are retained somewhat by the columns, but this interaction appears to be similar to that of the alkanes; non-specific yet some adsorption below the boiling points of the compounds. If one considers the resonance forms of the xylenes, one notes some polarity. It is known that the methyl group is weakly acti-

TABLE IX

RETENTION VOLUMES OF SOME SPECIAL SAMPLES (BENZENE TYPE) ON ALKALI METAL NITRATE COLUMNS

Conditions: temperature 120°; flow rate 60 cc/min; sample size 1.0 μ l.

	B.p.	V_R''				
		LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃
Benzene	80	a	a	a	a	a
<i>m</i> -Xylene	138	0.5	0.7	0.3	1.3	1.0
<i>p</i> -Xylene	139	0.5	0.7	0.3	1.2	1.1
<i>o</i> -Xylene	144	0.8	0.9	0.5	1.4	1.3
<i>m</i> -Chlorotoluene	162	1.0	2.0	1.5	3.1	2.6
<i>p</i> -Chlorotoluene	162	1.9	2.1	1.5	3.2	2.6
Benzylamine	185	14.7	7.4	5.7	10.4	8.5
<i>m</i> -Cresol	202	15.9	13.5	14.4	23.0	19.2
<i>p</i> -Cresol	202	16.4	18.4	14.0	23.4	19.1
Nitrobenzene	210	15.7	14.3	13.7	21.3	17.7

* a = elutes with air.

vating (*i.e.*, electron releasing) yet the reactivity is only slightly greater than benzene to substitution.

m-Chlorotoluene and *p*-chlorotoluene boil at slightly higher temperatures and under these conditions display only slightly greater adsorption. Both compounds have the slightly activating methyl group through hyperconjugation and the ring deactivating halogen present. Generally, one would consider the reactivities of these compounds to substitution below that of the xylenes. Their adsorption on these columns is very non-specific as Table IX shows.

The next higher boiling compound is benzylamine. Its retention volume is significantly greater than the chlorotoluenes; the difference in boiling points being 20°. The difference in boiling point between the xylenes and the chlorotoluenes was also 20° without a significant increase in retention volume. This may be explained by considering the resonance structures for benzylamine and the possibility of an intramolecular acid-base reaction. There appears to be strong adsorption when the phenyl group is rich with electron density.

TABLE X

RETENTION VOLUMES OF SOME SPECIAL SAMPLES (ANILINE TYPE) ON ALKALI METAL NITRATE COLUMNS

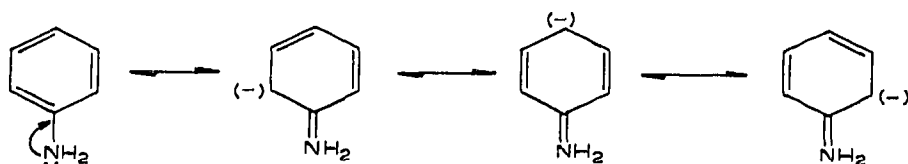
Conditions: temperature 120°; flow rate 60 cc/min; sample size 1.0 μ l.

	B.p.	V_R'				
		LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃
Aniline	184	6.9	5.4	5.6	10.2	8.3
<i>o</i> -Toluidine	199	11.8	10.2	10.3	15.5	12.7
<i>m</i> -Toluidine	203	13.8	10.5	12.5	18.4	15.6
<i>o</i> -Chloroaniline	208	15.7	12.9	13.0	20.4	17.6
<i>o</i> -Anisidine	225	30.2	22.6	25.3	36.8	31.7
<i>m</i> -Chloroaniline	229	35.1	26.7	28.3	42.2	35.7
2,4-Dimethylaniline	244	19.3	16.5	15.7	26.4	22.2

Let us now consider the cresols. *m*- and *p*-cresol boil 17° above benzylamine yet the retention volumes in all cases are greater for both compounds. The *para* isomer has a greater retention volume than the *meta* isomer. The cresols have two electron releasing groups which result in a significantly richer electron ring and their retention volumes are greater.

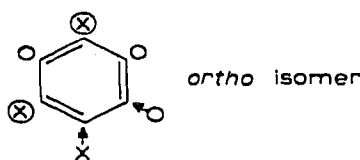
Nitrobenzene, boiling at 210°, is only 8° above the boiling point of the cresols. The retention volume is equal or slightly below that of the cresols. The nitro group is electron withdrawing and as a result we expect a decreased retention volume which is found when placed in proper boiling point perspective.

(ii) *Aniline type compounds*. Table X lists the aniline type compounds. The retention volumes are given in milliliters. The amino group itself is a strong group (see resonance structures below).



This fact coupled with the fact that sp^2 bonding to nitrogen requires coplanarity with the ring may account for the adsorption shown. Specifically, adsorption is governed by the interaction of the column packing with the now electron-rich ring.

o-Toluidine boils 15° above aniline, however, its retention volume is at least 50% greater. Perhaps the best explanation is the fact that the molecule now has two electron releasing groups on the ring. *m*-Toluidine boiling only 4° above the *ortho* isomer shows a significant increase in retention volume. This may be explained by the resonance structure below.



One finds increased electron density in four unsubstituted ring positions. Chemical substitution in an aromatic ring system of this type predominates *ortho* and *para* to the strongest electron releasing center (*i.e.*, to the amino group). In this structure two areas of high electron density and two of lesser electron density are found. The *meta* substituted product has three areas of extremely high density and one of low electron density. In the *meta* product, the two releasing groups supplement each other to produce areas of great density. This explains the increased adsorption of the *meta* product.

o-Chloroaniline boils 5° above *m*-toluidine, so one would expect a decreased adsorption. This is found to be true when we contrast the increase from *o*- to *m*-toluidine on KNO_3 , $RbNO_3$, and $CsNO_3$ columns with the increase found from *m*-toluidine to *o*-chloroaniline. The differences in going from *o*- to *m*-toluidine are (retention volume in ml) 2, 3, and 3, respectively. The differences from *m*-toluidine to *o*-chloroaniline (retention volume in ml) are 1, 2, and 2, respectively. The boiling point difference in both cases is 5°.

o-Anisidine, the next higher boiling compound, shows a greatly increased

retention volume. This may be accounted for by the fact that both groups are electron releasing and nitrogen (one lone pair of electrons) and oxygen (two lone pairs of electrons) are present. It is difficult to simply talk of adsorption because the column is 100° below the boiling point of the compound. One encounters a similar situation with *m*-chloroaniline. The next higher boiling compound is 2,4-dimethylaniline. Its retention volume is significantly below that of *o*-anisidine. This may be caused by steric hindrance.

TABLE XI

RETENTION VOLUMES OF SOME SPECIAL SAMPLES (PYRIDINE TYPE) ON ALKALI NITRATE COLUMNS
Temperature: 120°.

	<i>B.p.</i>	V_R'				
		<i>LiNO</i> ₃	<i>NaNO</i> ₃	<i>KNO</i> ₃	<i>RbNO</i> ₃	<i>CsNO</i> ₃
2-Picollime	128	1.0	0.9	0.4	1.4	1.1
3-Picollime	143	2.8	1.9	1.2	2.8	2.1
4-Picollime	143	3.6	2.3	1.3	3.0	2.4
Pyridlime	153	1.1	1.0	0.3	1.2	0.8

(iii) *Pyridime type compounds.* Table XI lists the pyridines in order of elution. The retention volumes are given in ml. The methyl group found in the three picolines is electron releasing. Its effect is most pronounced when it is located in the 4-position. This could be due to the electron density of the nitrogen atom; it appears that it represses the hyperconjugation effect of the methyl group. We can trace a trend that leads credence to this effect. Adsorption increases from the two position to the three position and is most pronounced in the four position.

II. Heats of adsorption

Chloride columns

A. Alkanes

The heat of adsorption for all alkanes is less than the heat of adsorption for the alcohols of the same carbon number, for example ΔH_a for *n*-hexane on the Li, Na, K, Rb, and Cs chloride columns, respectively is -6.71, -12.10, -8.42, -8.22, and -10.35; whereas *m*-hexanol on the same columns under identical conditions is -7.98, -11.80, -12.04, -9.45, and -11.52. Close examination of these data indicates that ΔH_a is least for *m*-hexane on all columns except NaCl. Examination of all the ΔH_a values for the alkanes studied shows that the heat of adsorption is the greatest on the NaCl column. Some trends, in order of decreasing heats of adsorption, are found in Table XII.

These data show that NaCl columns have the greatest affinity for all compounds and as the chain branching increases, CsCl columns display less adsorption for the molecule. 2,2-Dimethylbutane appears to violate this latter point, but reference to the actual values (KCl -2.75 kcal/mole and CsCl -3.07 kcal/mole) indicates that only a small difference exists hence, this "trend" appears to be real.

TABLE XII

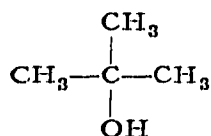
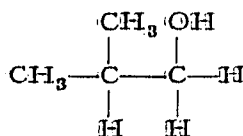
HEATS OF ADSORPTION (DECREASING) OF ALKANES ON ALKALI METAL CHLORIDE COLUMNS

<i>n</i> -Hexane	NaCl	>	CsCl	>	KCl	>	RbCl	>	LiCl
2-Methylpentane	NaCl	>	RbCl	>	KCl	>	CsCl	>	LiCl
3-Methylpentane	NaCl	>	KCl	>	RbCl	>	LiCl	>	CsCl
2,3-Dimethylbutane	NaCl	>	KCl	>	RbCl	>	LiCl	>	CsCl
2,2-Dimethylbutane	NaCl	>	RbCl	>	LiCl	>	CsCl	>	KCl

B. Alcohols

The alcohols present a rather interesting array of data. They are listed in order of decreasing heats of adsorption and are found in Table XIII.

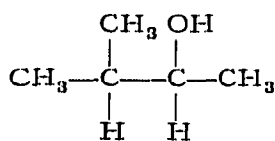
Considering first the butanols, the straight chain isomer elutes from the various columns in the following order: LiCl, RbCl, NaCl, CsCl, KCl. The molecule becomes more compact, as with *sec.*-butanol, the NaCl column displays least adsorptivity, the order being NaCl, LiCl, RbCl, CsCl, KCl; as we further condense the molecule, *e.g.* *tert.*-butanol and isobutanol, we observe least negative adsorption on NaCl. Refer closely to the structure of these two compounds in question.

*tert.*-Butanol

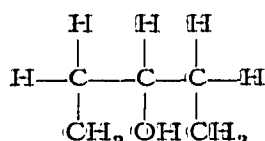
Isobutanol

In both cases a methyl group is present on either the same carbon atom to which the hydroxy group is bonded or in the α -position.

We can now consider the C_5 alcohols. The straight chain isomer on all columns displays strongly negative heats of adsorption; an interesting note is that isoamyl alcohol follows this trend and we find a methyl group located in the α -position. When we consider 3-methyl-2-butanol we discover a significantly less negative ΔH_a on NaCl columns; the same is true for 3-pentanol. If we look at the structures of these molecules, we can see a striking similarity to the butanol isomers, *i.e.*, in 3-methyl-2-butanol we find both an α -methyl group and a methyl group attached to the same carbon atom to which the OH group is bonded. In 3-pentanol we have two α -methyl groups.



3-Methyl-2-butanol



3-Pentanol

The data accumulated for the alcohols indicates purely physical adsorption is not simply the answer. It appears that some reaction occurs after adsorption and before desorption. One possible explanation is that some type of intermolecular hydrogen bonding occurs after adsorption which decreases the strength of the bond between the metal halide and the oxygen of the hydroxy group, hence, less energy would be required in the desorptive process. Another explanation could be the for-

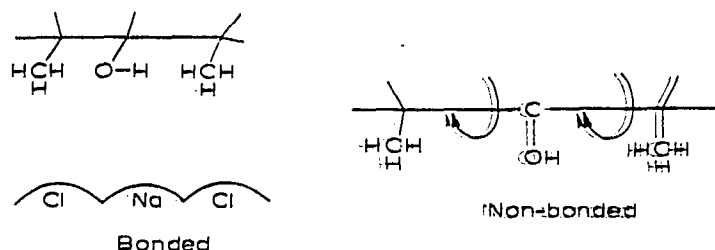
TABLE XIII

HEATS OF ADSORPTION OF THE C₄, C₅ AND C₆ ALCOHOLS ON ALKALI METAL CHLORIDE COLUMNS

	$-\Delta H_a^*$					
C ₄	<i>n</i> -Butanol	KCl -12.99	CsCl -10.88	NaCl - 9.88	RbCl - 9.30	LiCl - 8.43
	<i>sec.</i> -Butanol	KCl -15.39	CsCl -13.92	RbCl - 9.49	LiCl - 7.02	NaCl - 6.54
	<i>tert.</i> -Butanol	CsCl b	RbCl -15.45	KCl -14.89	LiCl - 9.84	NaCl a
	Isobutanol	CsCl -12.96	KCl -11.86	RbCl - 8.44	LiCl - 5.57	NaCl a
C ₅	<i>n</i> -Amyl alcohol	NaCl -13.21	KCl -12.21	RbCl -11.34	CsCl -10.97	LiCl - 6.47
	Isoamyl alcohol	NaCl -14.50	KCl -12.21	CsCl - 9.12	RbCl - 8.21	LiCl - 6.71
	3-Methyl-2-butanol	CsCl b	KCl -18.19	RbCl -11.74	LiCl -10.37	NaCl a
	3-Pentanol	LiCl -17.71	KCl -14.79	CsCl -12.96	RbCl - 9.92	NaCl a
	2,2-Dimethylpropanol	CsCl -13.23	KCl -12.85	NaCl -10.90	RbCl - 9.54	LiCl - 9.46
C ₆	<i>n</i> -Hexanol	KCl -12.04	NaCl -11.80	CsCl -11.52	RbCl - 9.45	LiCl - 7.98
	2-Hexanol	KCl -11.56	NaCl -10.98	CsCl - 9.74	RbCl - 9.16	LiCl - 7.48
	3-Hexanol	LiCl -23.63	NaCl -14.44	KCl -11.86	CsCl -10.17	RbCl - 8.61
	4-Methylpentanol	NaCl -11.53	CsCl - 9.92	RbCl - 9.87	LiCl - 9.63	KCl - 9.23
	3-Methylpentanol	LiCl -15.03	KCl -11.29	NaCl -10.98	CsCl - 9.73	RbCl - 8.61
	2-Methylpentanol	KCl -12.54	NaCl -12.07	CsCl -10.81	RbCl - 8.36	LiCl - 6.90
	2-Methyl-2-pentanol	KCl -12.54	RbCl - 9.64	CsCl - 9.54	LiCl - 8.78	NaCl - 6.63
	2-Methyl-3-pentanol	RbCl -18.19	CsCl -10.22	KCl - 9.37	LiCl - 7.61	NaCl - 1.23
	4-Methyl-2-pentanol	NaCl -12.00	KCl -11.30	CsCl -10.22	RbCl - 8.61	LiCl - 7.48
	3-Methyl-3-pentanol	NaCl -13.21	KCl -11.63	RbCl -10.63	CsCl - 9.93	LiCl - 6.71
	3-Methyl-4-pentanol	KCl -11.32	NaCl -10.44	RbCl - 9.74	CsCl - 9.69	LiCl + 2.07

* a = no reproducible data; b = eluted with air at two temperatures of investigation.

mation of alcoholates, the ΔH_f of which are sensitive to the stereochemistry of the alcohol. Energies usually associated with hydrogen bonding are of the order of magnitude tabulated for these alcohols. Hydrogen bonding is a possible explanation because the attraction of the anion for the δ^+ portion of the sample causes a decrease in the distance between the hydroxy group and the adjacent methyl groups. For example:



Another possible explanation is that NaCl columns may be porous enough to permit some of these more condensed structures to enter crystalline voids; all the compounds displaying the least negative ΔH_a values have similar structures except for the length of the chains, which should have little effect. The governing factor should be the width of the sample. In this case one would expect some anion attraction for the δ^+ portion of the molecule as well as cation attraction for the oxygen. Consequently, one would predict a greater negative heat of adsorption because of greater bond formation. We observe small ΔH_a values on NaCl columns with a number of alcohol samples.

Consider for a moment the alkanes. In all cases, greater adsorption was on the NaCl column. This suggests that some type of "hydrogen bonding" occurs, between the anion and the alkane portion of the molecule. It appears then that two different types of bonding could occur with the alcohols; some reaction between the hydroxy group and the cation, and some reaction between the alkane portion of the molecule.

C. Other sample types

Another group of compounds that has been studied shows some interesting trends. Aniline and some of its derivatives are found in Table XIV. All have significantly greater heats of adsorption than the alkanes; the least being -13.09 kcal/mole and the greatest -17.32 kcal/mole. Tabulation is in order of decreasing heats of adsorption.

Considering aniline as the standard the introduction of an electron releasing group (chloride) causes less adsorption. Ring activating groups (methoxy and methyl) due probably to their ability to release electrons cause greater adsorption. This is possibly due to the fact that these groups either increase or decrease the availability of the lone pair of electrons on the nitrogen atom; or possibly because they increase or decrease the electron density of the π complex of the aromatic nucleus. Steric effects, especially from *ortho* substitution, will have an effect on the adsorption of these type of compounds.

We can now look at the *meta* derivatives and employ the same technique. We find *m*-chloroaniline displays less adsorption than its *ortho* analogue and *m*-methyl-aniline again displays less adsorption than its *ortho* analogue.

Before discussing a possible rationale for these facts we will consider 2,4-

TABLE XIV

HEATS OF ADSORPTION OF SOME SPECIAL SAMPLES ON ALKALI METAL CHLORIDE COLUMNS

	<i>B.p.</i>	$-\Delta H_a$				
Aniline	184	LiCl -16.16	CsCl -14.19	RbCl -13.16	NaCl -13.09	KCl -12.13
<i>o</i> -Chloroaniline	208.8	LiCl -16.74	RbCl -13.01	KCl -12.99	CsCl -12.60	NaCl -11.97
<i>o</i> -Anisidine	225	LiCl -16.23	RbCl -14.74	KCl -14.16	NaCl -13.29	CsCl -12.94
<i>o</i> -Toluidine	199.8	LiCl -17.32	CsCl -15.27	NaCl -14.20	KCl -13.85	RbCl -13.94
2,4-Dimethylaniline	216	CsCl -15.44	NaCl -15.41	LiCl -14.43	KCl -14.07	RbCl -14.03
<i>m</i> -Chloroaniline	230	RbCl -14.31	LiCl -13.05	KCl -13.04	NaCl -12.81	CsCl -12.32
<i>m</i> -Chlorotoluene	162	NaCl -15.65	LiCl -15.45	CsCl -14.66	KCl -13.53	RbCl -13.23

dimethylaniline. Looking at the molecule itself we have an *ortho* and *para* electron releasing group to the amino group. We expect an enhanced effect of these electrons and consequently greater adsorption than with any compound thus far considered. This occurs because the π system is just as sensitive to substituents as the amino group.

These data suggest that the interaction between the column packing and the molecule is not simply interaction between the nitrogen's electrons. Rather it could be the sum of two effects; first, interaction with the electrons of the nitrogen and second, interaction between the electrons of the aromatic molecule and the cation. If chemisorption is involved, the "complex" formed would probably be very specific and not involve two types of bonding. If we look closely at the values of 2,4-dimethylaniline on all columns (Table IV) they are of the same order of magnitude indicating very non-specific adsorption.

We are now in a position to discuss *o*- and *m*-toluidine. Both groups present on the ring are electron releasing, *i.e.*, they donate electrons to the ring. We expect, and find that the greatest enhancement is with the *ortho* substituents. This indicates that a very strong complex is formed. This increased adsorption is expected to decrease if we place the substituents in the *meta* position to one another. We find in this case stronger activating groups would increase significantly the electron density at the *ortho* and *para* positions. Weaker activating groups would increase electron density to a lesser extent at these positions.

SUMMARY

Retention volume

- (1) Alkali nitrate columns retard elution greater than alkali chloride columns.
- (2) Retention volume generally follows boiling point. If two compounds have the same boiling point, the more polar compound has the greater retention volume.

- (3) Chain branching, through decreased polarity, reduces retention volume.
(4) Electron releasing groups enhance adsorption; electron withdrawing hinder it.
(5) *Ortho* substituents cause stronger effects than *meta* substituents.

Heats of adsorption

Adsorption of solutes on alkali metal chlorides and nitrates is physical adsorption under these conditions of investigation. Heats of adsorption increase as the polarity or electron densities increase.

Conclusion

Inorganic salts show promise as selective adsorbents in GSC. This study shows that electronic and polarization considerations dictate elution order. It also demonstrates "physical adsorption" is the predominant process and not chemisorption. Alkali metal chlorides and nitrates can be used as adsorbents, conveniently, in GSC. Their analytical importance is not stressed because of their low elution volumes.

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