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EVIDENCE OF INTERACTIONS OF ORGANIC SORBATES WITH TRANSITION METAL HALIDES IN GAS-SOLID CHROMATOGRAPHY USING THERMODYNAMICS AND INFRARED STUDIES

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SUMMARY

Investigations were conducted to study the separations obtained using anhydrous cobalt(II) and manganese(II) chlorides as gas chromatographic packings and the extent to which their surface effects controlled or influenced these separations. Sorbates which varied in the degree of π -electron distribution, some having isolated π -bonds with varying electron density, were studied. Others consisted of conjugated π -electron systems (aryl systems). The order of elution of these compounds on both packings was correlated with the degree of π -electron distribution. Compounds with isolated π -bonds were retained more strongly than conjugated systems. Interaction appeared to be a function of π -electron density of the adsorbate and the electron deficient qualities of the transition metal salt. The thermodynamic functions ΔH , ΔS and ΔG were calculated by a computer program at temperatures of 50-150° and 29-60°. Heats of adsorption were less than 15 kcal/mole and entropies were in the range that could be predicted on the basis of vaporization, *i.e.*, no evidence of chemisorption could be demonstrated thermodynamically in the chromatographic system. Non-chromatographic adsorption was studied by IR spectroscopy. Spectra obtained were identical for the same sorbate on either salt. Cobalt(II) chloride appeared more selective than manganese(II) chloride despite the larger surface area of the latter.

INTRODUCTION

The transition metal halides cobalt(II) and manganese(II) chlorides were studied for possible application as gas chromatographic packings. This application was based upon a potential affinity of olefinic and aryl compounds (sorbates) for the electron-deficient d-orbitals of the metal cation of the sorbent. Numerous papers have appeared describing the adsorption of various compounds on transition metal salts and metal oxides¹⁻⁷. In gas chromatography, a familiar application has been the use of silver nitrate to separate various olefinic compounds⁸⁻¹². More recently, Gil-Av and Schurig¹³ reported rhodium coordination compounds to separate mono-

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olefins, while Schurig *et al.*¹⁴ discussed the use of rhodium carboxylates as stationary phases for the analysis of ethers, ketones, esters and alkenes.

The mechanism of the adsorption process in a dynamic system, such as gas chromatography, has not been clearly understood. Terms such as reversible and irreversible chemisorption or physical adsorption seem inadequate. Static studies, such as those of Bennett¹⁵ and Dent and Kokes², have determined that bonding can occur between a transition metal salt and a sorbate possessing π -electron density. On the other hand, Snyder¹⁶ has observed that adsorption can occur in a dynamic system with large adsorption energies and apparent electron transfer between sorbate and sorbent but no conventional bonds are formed. Guha and Janák¹⁷ described the same interactions as charge-transfer complexes discussing the application of infrared spectroscopy as an aid in establishing the nature of the interaction in terms of changes in the structural characteristics of the sorbate.

In this investigation, static studies using infrared spectroscopy were used to establish an interaction between the sorbate and the anhydrous transition metal halide (sorbent) at room temperature. The sorbate was then chromatographed using the transition metal halide as a packing at column temperatures near the boiling point of the sorbates and at room temperature. Thermodynamic values such as the enthalpy and entropy of adsorption were calculated at normal gas chromatographic temperatures and compared to those calculated at temperatures where interaction was known to occur.

MATERIALS AND EQUIPMENT

A Varian Model 1840-1 gas chromatograph equipped with dual columns and dual flame ionization detectors (FID) was employed throughout this investigation. Helium was the carrier gas; breathing air and hydrogen served as the combustion medium for the detector. The carrier gas flow-rate was maintained at 14–15 ml/min. All three gases were dried using calcium chloride and a molecular sieve. Columns were constructed from 0.25-in. O.D. Pyrex glass. The gas chromatographic studies conducted near room temperature employed columns 10–28 cm in length. These columns were fitted with water jackets and the temperature regulated using a Haake Model FJ constant-temperature circulator. With this arrangement, the temperature could be maintained to within $\pm 0.5^\circ$. For higher-temperature studies, the columns were 6 ft. in length. As column temperatures were in the range 50–150°, a YST Model 42SF telethermometer (Yellow Springs Instrument Co.) was used to monitor temperature, independent of the instrument pyrometer. Cobalt(II) chloride was obtained from Research Organic/Inorganic Chemical Corp. (Belleville, N.J., U.S.A.) and manganese(II) chloride was obtained from K and K Labs. (Plainview, N.Y., U.S.A.) (all packings were ground and sieved to 60–80 mesh). Sorbates were chromatographed as 1% (v/v) solutions in methylene chloride (reagent grade). A few solutions were prepared in *n*-octane and are noted where appropriate.

EXPERIMENTAL

Sample size

Because of the number of samples studied, adsorption isotherms were not

determined. However, repeated injections over a range of 0.1–1.0 μl gave the same retention time for each sorbate indicating the sorbates were studied over the linear part of the adsorption isotherm.

Curing conditions

Both cobalt(II) and manganese(II) chlorides are hygroscopic. To assure the anhydrous state, both salts were allowed to equilibrate under ambient conditions in the laboratory, and thermally analyzed using a Perkin-Elmer DSC-1B differential scanning calorimeter. The samples were scanned in open aluminum dishes using a dry nitrogen purge. After a complete scan (50–475°), the temperature was re-set without removing the sample and the thermal scan repeated. For both salts, endotherms were observed during the first scan but were absent during the re-scan. The interpretation was that the endotherms observed were due to loss of volatiles, presumably water. Packed columns were cured at the highest temperature defined by the endotherms. For manganese(II) chloride, the curing temperature was 230° and for cobalt(II) chloride 190°.

Surface area

Surface area was determined by Micromeritics Instrument Co. using an Orr Model 2100A surface area–pore volume analyzer. Manganese(II) chloride (anhydrous) was found to have a surface area of 5.49 m^2/g and cobalt(II) chloride (anhydrous) had a surface area of 3.24 m^2/g .

Thermodynamic functions

The heat of adsorption (ΔH_a) and the entropy of adsorption (ΔS_a) were calculated by a computer program using at least three different column temperatures (and retention volumes). Using the same raw data, the program simultaneously calculated and plotted the least-squares data. When the heats of adsorption calculated from both slopes were compared, the correlation coefficient was greater than 0.98 in the case of every sample studied.

Infrared studies

Potassium bromide (200 mg) was mixed with a ground sample (2–4 mg) of cobalt(II) chloride or manganese(II) chloride. The mixture was transferred to a weighing boat and placed in the oven of the gas chromatograph, where it was cured at 200° for a period of 20–30 min. The boat containing the mixture was removed, placed in a vacuum desiccator and allowed to cool. In a low-humidity room, the desiccator lid was removed and the mix was saturated with the organic compound (sorbate) to be studied. The lid was replaced and the desiccator was evacuated for 2–3 min. The vacuum was broken, the mix was stirred with a spatula so that fine particles were obtained and the vacuum was renewed for another 1 min. Some moisture was adsorbed during this procedure but did not cause interference in the pertinent infrared regions. The mix was immediately transferred to a circular pellet mold and compressed at high pressure so that a translucent pellet was obtained. The infrared spectrum was determined over the range 4000–250 cm^{-1} using a Perkin-Elmer Model 521 infrared spectrophotometer.

TABLE I
HEATS OF ADSORPTION AND ENTROPIES FOR A SERIES OF COMPOUNDS ON MANGANESE(II) AND COBALT(II) CHLORIDE
COLUMNS AT NORMAL GC TEMPERATURES

Sample	CoCl ₂ *		MnCl ₂ *				
	B.p. (°C)	ΔH (kcal/mole)	ΔS (cal/mole)	Column temp. (°C)	ΔH (kcal/mole)	ΔS (cal/mole)	Column temp. (°C)
<i>n</i> -Pentane**	36.2	-8.29	-28.4	50-80	-5.61	-19.5	70-95
<i>n</i> -Hexane**	69.0	-8.21	-26.0	50-80	-8.09	-24.7	70-95
<i>n</i> -Heptane	98.4	-9.56	-28.0	50-80	-9.14	-25.9	70-95
<i>n</i> -Octane	125.8	-10.3	-28.2	50-80	-11.2	-29.6	70-95
<i>n</i> -Nonane	150.8	-11.5	-29.7	50-80	-	-	-
1-Chloropentane	108.2	-11.3	-31.2	50-80	-	-	-
2-Chloropentane	96.5	-11.6	-32.9	50-80	-11.7	-33.5	70-95
3-Chloropentane	104.5	-8.59	-23.8	50-80	-11.3	-32.4	70-95
1-Chlorobutane	78	-9.36	-27.5	50-80	-11.8	-33.2	70-95
2-Chlorobutane	68	-9.40	-28.3	50-80	-7.85	-24.1	70-95
1-Chlorobutene-1	63.5	-10.3	-32.5	50-80	-11.3	-32.6	70-95
2-Chlorobutene-1	58.5	-10.4	-32.8	50-80	-11.9	-34.2	70-95
4-Chlorobutene-1	75	-10.9	-32.3	50-80	-13.8	-36.2	70-95
Pentene-1**	30.0	-5.58	-19.3	50-80	-11.0	-31.0	70-95
Pentyne-1***	40	-10.2	-27.8	50-80	-	-	-
Hexene-1	63.5	-8.34	-26.0	50-80	-12.2	-33.4	70-95
Hexyne-1***	71.5	-13.6	-39.1	50-80	-	-	-
Benzene	80	-10.7	-31.9	50-80	-13.2	-34.3	70-95
Chlorobenzene	132	-10.7	-29.5	50-80	-13.6	-34.8	70-95
Toluene	111	-11.8	-32.7	50-80	-13.2	-31.9	109-128
<i>o</i> -Xylene	144	-12.6	-32.7	50-80	-14.1	-31.0	140-160
<i>m</i> -Xylene	139	-12.3	-31.9	50-80	-14.2	-31.6	140-160
<i>p</i> -Xylene	138	-11.6	-30.2	50-80	-14.3	-31.7	140-160

* 6 ft. × 0.25 in. O.D.

** Data reported in previous work¹.*** Solution in *n*-octane.

TABLE II
HEATS OF ADSORPTION AND ENTROPIES FOR A SERIES OF COMPOUNDS ON MANGANESE(II) AND COBALT(II) CHLORIDE COLUMNS AT LOW TEMPERATURE BY GC

Sample	B.p. (°C)	CoCl ₂ *		MnCl ₂ *	
		ΔH (kcal/mole)	ΔS (cal/mole)	ΔH (kcal/mole)	ΔS (cal/mole)
<i>n</i> -Pentane**	36.2	0	0	-6.17	-23.1
<i>n</i> -Hexane**	69.0	-12.6	-40.7	-8.88	-29.0
1-Chlorobutane	78	-13.8	-38.8	-9.55	-27.2
1-Chlorobutene-1	63.5	-12.5	-38.9	-8.97	-28.0
4-Chlorobutene-1	75	-15.0	-42.4	-10.4	-29.0
Pentene-1	30.0	-	-	-7.98	-26.5
Hexene-1	63.5	-	-	-10.2	-31.5
Benzene	80	-11.6	-33.9	-9.97	-27.3
Pentyne-1	40	-14.0	-38.0	-11.8	-33.9
Hexyne-1	71.5	Not eluted	Not eluted	-12.4	-35.3
Cyclohexane	81.4	-12.8	-42.6	-7.16	-24.5

* 28 cm × 0.25 in. O.D.

** Solution in *n*-octane.

TABLE III
DIFFERENCE BETWEEN HEATS OF ADSORPTION AND ENTROPIES ON REGULAR LENGTH (6 ft.) COLUMNS OF MANGANESE(II)
AND COBALT(II) CHLORIDE AND SHORT (28 cm) COLUMNS

Sample	B.p. (°C)	CoCl ₂ reg. — CoCl ₂ short		MnCl ₂ reg. — MnCl ₂ short		CoCl ₂ reg. — MnCl ₂ reg.		CoCl ₂ short — MnCl ₂ short	
		Δ (ΔH)	Δ (ΔS)	Δ (ΔH)	Δ (ΔS)	Δ (ΔH)	Δ (ΔS)	Δ (ΔH)	Δ (ΔS)
<i>n</i> -Pentane	36.2	—	—	+0.56	+3.6	-2.67	-8.9	—	—
<i>n</i> -Hexane	69.0	+4.39	+14.7	+0.79	+4.3	-0.12	-1.3	-3.72	-11.7
1-Chlorobutane	78	+4.40	+11.3	+2.55	-6.0	+2.44	+5.7	-4.25	-11.6
1-Chlorobutene-1	63.5	+2.20	+6.4	+2.33	-4.6	+1.00	+0.1	-3.53	-10.9
4-Chlorobutene-1	75	+4.10	+10.1	-3.40	-7.2	+2.90	+3.9	-4.60	-13.4
Pentene-1	30.0	—	—	-3.02	-4.5	+5.42	+11.7	—	—
Hexene-1	63.5	—	—	-2.00	-1.9	+3.86	+7.4	—	—
Benzene	80	+0.90	+2.0	-0.70	+1.4	+2.50	+2.4	-1.63	-6.60
Pentyne-1	40	+6.43	+14.4	—	—	—	—	-2.20	-4.10
Hexyne-1	71.5	—	—	—	—	—	—	—	—
Cyclohexane	81.4	—	—	—	—	—	—	-5.64	-18.1

DISCUSSION

Thermodynamic studies

Table I lists the heats of adsorption (kcal/mole) and the entropies of adsorption (cal/mole) for a series of compounds chromatographed at temperatures higher than 50°. At these temperatures, complexes of the type that might form between olefins and transition metal salts resulting from chemisorption should show minimum stability¹⁸. The magnitude of the heats of adsorption (< 14–15 kcal/mole)¹⁹ did not indicate chemisorption. In addition, entropies of adsorption were within the range that could be expected from simple vaporization (as might be calculated from Trouton's rule assuming an ideal gas). The slightly higher thermodynamic values observed using manganese(II) chloride were most likely due to the greater surface area of manganese(II) chloride as compared with cobalt(II) chloride.

Table II lists the heats of adsorption and entropies of adsorption for a series of compounds chromatographed over a temperature range of 29.5–70.0°. As before, the data in Table II did not indicate chemisorption. However, differences were noted between the thermodynamic values calculated on short columns (lower temperatures). These data are shown in Table III. The data indicated that manganese(II) chloride was thermodynamically the stronger adsorbent at temperatures higher than 50–60°. However, at temperatures less than 50–60°, cobalt(II) chloride appeared to be the stronger adsorbent, despite the significantly greater surface area of manganese(II) chloride. Clearly, the questions involved regarding specific interactions and non-specific interactions, as described by Brookman and Sawyer²⁰, are too complex to explain using thermodynamics alone. One could easily get entangled in rationalizing differences between polarities, polarizabilities and the stereochemistry of the adsorbate relative to the adsorbent. These distinctions are always open to challenge depending on one's interpretation of the data.

TABLE IV
RETENTION ORDER OF A SERIES OF COMPOUNDS ON CoCl₂

<i>Peak number</i>	<i>Compound</i>	<i>B.p. (°C)</i>	<i>Dipole moment (Debye)*</i>
1	Cyclohexane	81.4	0
2	Benzene	80.1	0
3	Chlorobenzene	132	1.69
4	Toluene	111	0.36
5	<i>p</i> -Xylene	138	0
6	<i>o</i> -Chlorotoluene	159	1.56
	<i>m</i> -Chlorotoluene	162	
7	Cumene (isopropylbenzene)	153	0.79
8	<i>tert</i> -Butylbenzene	169	0.83
9	<i>m</i> -Xylene	139	
10	<i>o</i> -Xylene	144	0.62
11	<i>n</i> -Butylbenzene	183	
12	Cymene (isopropyltoluene)	174	
13	1,3,5-Trimethylbenzene	165	
14	1,2,4-Trimethylbenzene	169	

* From ref. 24.

Infrared studies

Dent and Kokes² used infrared spectroscopy to study the adsorption of propylene on zinc oxide. They interpreted shifts in frequencies attributable to propylene π -bonds as indicative of adsorption. Bennett¹⁵ observed the loss of triple bond character (by IR spectroscopy) when acetylene was complexed with carbonyl complexes of cobalt and manganese. He postulated a charge transfer from the π -orbital of the ligand to the metal orbitals. In this investigation, when *n*-hexane was placed in contact with cobalt(II) chloride using the technique described, no additional bands were observed other than those of the salt alone. On the other hand, the adsorption of hexene-1 was evidenced by the appearance of C-H stretching bands at 2850–2950 cm^{-1} . However, no other bands corresponded to those found with pure liquid hexene-1. In addition, the spectrum did not resemble pure liquid *n*-hexane in any way; some new species has formed. When the experiment was repeated using hexyne-1, adsorption was again evidenced by the presence of C-H stretching bands in the range 2850–2950 cm^{-1} . However, the strong bands attributable to a triple bond, *i.e.*, in the region 330 cm^{-1} and 2117 cm^{-1} , were absent. The spectrum bore no resemblance to either *n*-hexane or hexene-1. The spectra obtained for the same sorbates on manganese(II) chloride were identical with those obtained using cobalt(II) chloride. The π -electrons of hexene-1 and hexyne-1 seemed essential for adsorption. No adsorption was observed on either salt using benzene, toluene, chlorobenzene or diethyl ether. The fact that benzenoid compounds showed no adsorption (or weak adsorption at best) using the technique described was compatible with reported observations²¹ that conjugated systems formed significantly weaker complexes due to the dispersed nature of their

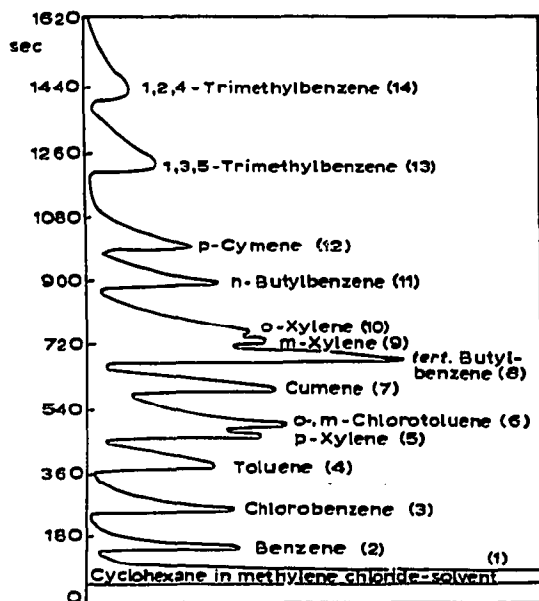


Fig. 1. Series of compounds chromatographed on CoCl_2 (6 ft.). Sample: 0.3 μl . Column temperature: 115–190°, programmed at 6°/min. Injection port: 125°. Detector: 155°. Helium flow-rate: 14.8 ml/min. Hydrogen flow-rate: 16.4 ml/min. Air flow-rate: 150 ml/min.

π -electron density. The adsorption of hexyne-1 was studied by the technique just described using silver nitrate in place of cobalt(II) chloride or manganese(II) chloride. The spectrum indicated that adsorption occurred by the appearance of C-H stretching bands in the region 2850–2950 cm^{-1} , although the strong bands attributable to a triple bond were absent. Hence the infrared spectrum obtained for hexyne-1 on silver nitrate resembled those spectra obtained for the adsorption of hexyne-1 on cobalt(II) or manganese(II) chloride.

Retention order

Table IV lists the elution order of a series of compounds chromatographed as a mixture on a column of cobalt(II) chloride. The chromatogram is shown in Fig. 1. Table V lists the elution order of the same series of compounds chromatographed on manganese(II) chloride. The corresponding chromatogram is shown in Fig. 2. Cyclohexane, benzene, chlorobenzene and toluene were eluted in the same order on both columns. The order could not be predicted from boiling point or dipole moment differences. However, Okamura and Sawyer²² had observed a similar elution order and attributed the phenomena to the influence of activating and deactivating groups on polar interactions between sorbate and sorbent. A deactivating group, such as chlorine, decreases the π -electron density of the benzene ring while activating groups, such as methyl, to some extent localize the π -electron density. The interaction occurred despite the fact that infrared analysis indicated no adsorption of these compounds at room temperature. It was possible that adsorption was not evidenced due to the limited sensitivity of the infrared technique. Snyder¹⁶ described this type of adsorption as polar adsorption, while Brookman and Sawyer^{20,23} referred to the same phenomenon as a specific interaction which defines a substrate that couples with a specific center of the adsorbate. The π -electron character of the adsorbate plus a steric effect determines the degree of adsorption and hence the elution order. On cobalt(II) chloride,

TABLE V
RETENTION ORDER OF A SERIES OF COMPOUNDS ON MnCl_2

Peak number	Compound	B.p. ($^{\circ}\text{C}$)	Dipole moment (Debye)*
1	Cyclohexane	81.4	0
2	Benzene	80.1	0
3	Chlorobenzene	132	1.69
4	Toluene	111	0.36
	<i>o</i> -Chlorotoluene	159	1.56
5	<i>m</i> -Chlorotoluene	162	
6	<i>p</i> -Xylene	138	0
	<i>m</i> -Xylene	139	
7	Cumene (isopropylbenzene)	153	0.79
8	<i>o</i> -Xylene	144	0.62
9	<i>tert.</i> -Butylbenzene	169	0.83
10	1,3,5-Trimethylbenzene	165	
11	<i>p</i> -Cymene	174	
	1,2,4-Trimethylbenzene	169	

* From ref. 24.

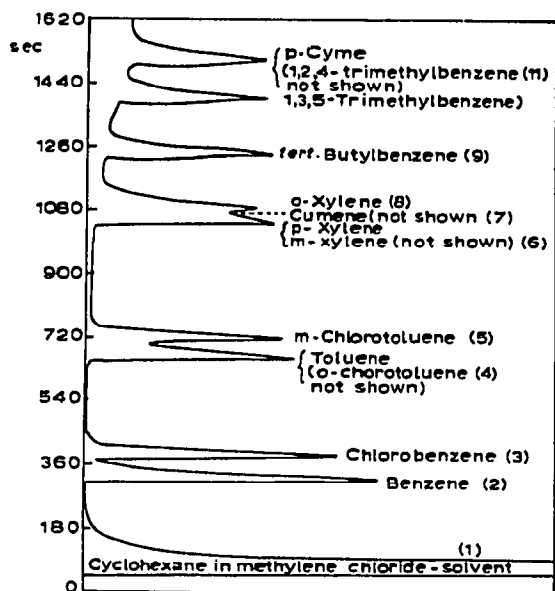


Fig. 2. Series of compounds chromatographed on $MnCl_2$ (6 ft.). Sample: 0.1 μ l. Column temperature: 100–200°, programmed at 4°/min. Injection port: 125°. Detector: 155°. Helium flow-rate: 14.5 ml/min. Air flow-rate: 150 ml/min. Hydrogen flow-rate: 16.4 ml/min.

p-, *m*- and *o*-xylene were eluted in the order of increasing electron localization, independent of the boiling point; the resolution was lower on manganese(II) chloride. The elution order suggested that cobalt(II) chloride was more selective than manganese(II) chloride relative to the π -electron density of the adsorbate, despite the smaller surface area of the cobalt(II) chloride.

Table VI shows the ratio of adjusted retention volume of a series of sorbates

TABLE VI

RATIO OF CORRECTED RETENTION VOLUME OF SELECTED COMPOUNDS RELATIVE TO *n*-HEXANE FOR SHORT COLUMNS OF COBALT(II) AND MANGANESE(II) CHLORIDE AT LOW TEMPERATURE

Compound	B.p. (°C)	$CoCl_2$		$MnCl_2$		
		10 cm, 29.5°	28 cm, 29.5°	28 cm, 49.5°	28 cm, 29.5°	28 cm, 49.0°
Cyclohexane	81.4	0.522	0.472	0.559	0.543	0.665
<i>n</i> -Hexane	69.0	1.0	1.0	1.0	1.0	1.0
<i>n</i> -Pentane	36.2	0.156			0.202	0.278
Benzene	80	5.33	6.26	6.36	12.48	13.43
1-Chlorobutane	78	16.9		16.3	7.10	8.77
1-Chlorobutene-1	63.5	2.25		1.95	1.63	1.95
4-Chlorobutene-1	75				8.52	9.46
Pentene-1	30	1.66		3.05	0.672	0.891
Hexene-1	63.5	3.78		7.54	2.62	3.24
Pentyne-1	40			34.6	10.72	7.94
Hexyne-1	71.5	17.67			15.13	9.91

relative to *n*-hexane at column temperatures near ambient. At temperatures lower than 40°, retention volumes were too large for practicality using cobalt(II) chloride columns that were longer than 10 cm. The data indicated that at low temperatures, cobalt(II) chloride was a significantly stronger adsorbent than manganese(II) chloride when the adsorbate contains π -electrons. The only exception was benzene. Because no region of high electron density exists in benzene, the molecule has a very large area for potential affinity to the adsorbent. As manganese(II) chloride has a large surface area, relative to cobalt(II) chloride, manganese(II) chloride has a statistical advantage for potential sites of interaction. The same is true of cyclohexane and *n*-hexane. Cyclohexane, owing to its configuration, cannot approach the active sites as well as *n*-hexane. Consequently, despite the higher boiling point of cyclohexane, it eluted before *n*-hexane. Cyclohexane was probably retained longer on manganese(II) chloride than on cobalt(II) chloride because of surface area differences as noted.

CONCLUSIONS

The results indicate that an interaction occurs between sorbates possessing π -electron density and the sorbents cobalt(II) and manganese(II) chlorides. This interaction can be used to separate sorbates varying in their degree of π -electron distribution. Thermodynamic calculations such as enthalpy and entropy of adsorption, traditionally employed to interpret the nature and degree of interaction, are inadequate. In this study, the difficulty arose primarily because differences in magnitude of thermodynamic values were not great enough to distinguish selectively various mechanisms of interaction or even that interaction did, in fact, occur. Instead, infrared spectroscopy was used to establish the fact that interaction involving π -electron density and the transition metal salt occurred in an ambient, static study. These results were used to rationalize the behavior of the same sorbate-sorbent interaction in a dynamic gas chromatographic system.

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