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USE OF TRANSITION METAL CHLORIDES AS SALT MODIFIERS IN GAS–SOLID CHROMATOGRAPHY

NELSON H. C. COOKE* and EUGENE F. BARRY**

Department of Chemistry, Lowell Technological Institute, Lowell, Mass. 01854 (U.S.A.)
and
BARTON S. SOLOMON
Department of Chemistry, Merrimack College, Andover, Mass. 01845 (U.S.A.)
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SUMMARY

This work focuses on the modification of silica gel with several transition metal salts. The chlorides of Mn(II), Co(II) and Zn(II) were employed as modifiers. The gas–solid chromatographic behavior of several alkanes, alkenes and aromatic sorbates is discussed in terms of sorbate–sorbent interactions and is compared to their interaction with unmodified silica gel. Salt modification adds another dimension to column parameters which may be varied to achieve selective analytical separations.

INTRODUCTION

Active solid adsorbents such as silica gel and alumina have been routinely used in liquid–solid chromatography. The utilization of these adsorbents in gas–solid chromatography (GSC) has been confined to the analysis of light hydrocarbons and permanent gases because of nonlinear adsorption isotherms yielding asymmetrical elution peaks. If the adsorbent is coated with an inorganic salt, the active surface area of the adsorbent is reduced and becomes more homogeneous; thus, more symmetrical elution peaks with lower retention times can be observed for weakly interacting adsorbates[1–3].

There has been a continued interest in the area of salt-modified adsorbents as Sawyer and coworkers[4–7] have extended the usefulness of GSC by achieving selective analytical separations with modified adsorbents. With salt modification of alumina, silica gel and porous silica beads, Sawyer *et al.* have demonstrated that great selectivity is noted in the separation of isomeric mixtures. In particular, the sorbate–salt-modified adsorbent interaction is a composite of nonspecific and specific contributions with the latter contribution dependent upon the π-electronic nature and geo-

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metrical configuration of the sorbate. For example, with aromatic hydrocarbons, the substitution of electron-donating or electron-withdrawing groups greatly influences the interaction with the salt-modified adsorbent whereas with alkenes, the *trans*-isomer is eluted before the *cis*-isomer. The nature of the salt-modifying agent and the coated adsorbent has been shown to affect sorbate–adsorbent interaction.

The present GSC study focuses upon silica gel which has been coated with the chlorides of Ca(II), Mn(II), Co(II), and Zn(II). The cations of these salts differ in the number of available "$3d$" orbitals and possess electronic configurations of $3d^0$, $3d^5$, $3d^7$ and $3d^{10}$, respectively. Since these salts are Lewis acids, electron-donating-type substances should undergo surface complexation to varying degrees with these salts. This technique provides an additional path for the achievement of selective analytical separations.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 900 gas chromatograph equipped with dual hydrogen flame ionization detectors was employed in the investigation. The flow-rates of the carrier gas (nitrogen) and hydrogen were maintained at 40 ml/min while the air flow-rate was held constant at 375 ml/min. A Leeds and Northrup Model W/L strip chart recorder with a chart speed of 30 in./h and a 1-mV range was used to record the chromatograms. The carrier gas was dried prior to entering the chromatograph by passage through a 5 Å molecular sieve and drierite gas filter. Sorbate samples were injected as vapors with a 10-μl Hamilton syringe after a small amount of pure liquid had been placed in a 5-ml tightly sealed vial.

Column preparation

The salts used as modifiers were the reagent grade chlorides of Mn(II), Co(II), Zn(II), and Ca(II). Thermogravimetric analysis indicated that hydrated water is removed at the conditioning temperature of 250 °C. Davidson 62 silica gel (80–100 mesh) was employed as the adsorbent and our improved coating procedure has recently been reported[8,9]. The amount of salt added provided a 10% by weight coating of the salt in each case on the adsorbent. The coated adsorbent was then placed in a preheated oven at 250 °C for 3 h.

After activation the adsorbents were resieved and packed into preweighed 3-ft. sections of 1/8-in.-O.D. stainless-steel tubing which had been previously rinsed consecutively with hexane, acetone and methylene chloride. After each column had been packed, the column was installed in the gas chromatograph and conditioned at 250 °C for 24 h with a nitrogen flow-rate of 40 ml/min.

Procedure

Retention volumes of the sorbates were measured at 205 °C, 220 °C, 235 °C and 250 °C on each column. For a given sorbate five injections were made at each temperature. The dead volume of the system was assumed to be equal to the retention volume of methane at 250 °C. Since the chromatographic peaks exhibited no tailing and were independent of injected sample volume, measurements were conducted on the linear region of the adsorption isotherm; thus, significant thermodynamic data

can be elucidated. On each column, the heat of adsorption of an adsorbate, ΔH_a, was calculated by plotting the logarithm of corrected retention volume *vs.* $1/T$, where T is the column temperature in $°K$ and the slope of the plot equal to $-\Delta H_a/2.303R$. The free energy of adsorption is related to the distribution constant, K, by the relation

$$\Delta G_a = -RT \ln K = -RT \ln V_s^T$$

where ΔG_a refers to the nonstandard state free energy of adsorption and V_s^T is the specific retention volume at a given temperature, $T(°K)$. The corresponding entropy of adsorption, ΔS_a, is obtained by

$$\Delta S_a = \frac{\Delta H_a - \Delta G_a}{T}$$

RESULTS AND DISCUSSION

The retention volumes for a number of hydrocarbons and substituted benzenes have been measured on silica gel and 10% salt-modified silica gel packings. In GSC the net retention volume, V_N, can be converted to the specific retention volume at a given temperature, V_s^T by dividing by the surface area of the adsorbent, A_s. The specific retention volume at a given column temperature for a given sorbate-sorbent pair is also equal to the distribution constant, K

$$\frac{V_N}{A_s} = V_s^T = K = \frac{C_{(S)}}{C_{(G)}} \text{ (ml/m}^2\text{)}$$

where $C_{(S)}$ and $C_{(G)}$ are the concentrations of sorbate in solid and gas phases, respectively. The variation of V_s^T from sorbent to sorbent for the same sorbate molecule indicates differences in distribution behavior, due solely to changes in the adsorbent. In Table I, V_s^T values at 235 °C are presented for both aromatic and aliphatic sorbate-sorbent pairs. In all cases, modification of the silica gel surface with a salt decreases

TABLE I

V^T VALUES AT 235 °C (ml/m²)

Compound	B.p. (°C)	Silica gel	10% MnCl₂	10% CoCl₂	10% ZnCl₂	10% CaCl₂
Benzene	80	0.0923	0.0720	0.0615	0.0605	0.0617
Fluorobenzene	85	0.0840	0.0729	0.0636	0.0615	0.0617
Toluene	110	0.2094	0.1566	0.1319	0.1233	0.1215
Chlorobenzene	132	0.1720	0.1539	0.1269	0.1237	0.1193
Bromobenzene	155	0.2685	0.2281	0.1985	0.1888	0.1817
Ethylbenzene	136	0.3901	0.2756	0.2417	0.2199	0.2117
Cumene	152	0.6420	0.4417	0.3929	0.3515	0.3098
n-Pentane	36	0.0168	0.0159	0.0144	0.0136	0.0123
1-Pentene	30	0.1516	0.0273	0.0335	0.0250	0.0199
n-Hexane	69	0.0336	0.0317	0.0257	0.0259	0.0225
1-Hexene	64	—	0.0485	0.0574	0.0490	0.0345
n-Heptane	98	0.0606	0.0512	0.0473	0.4010	0.0396
1-Heptene	93	—	—	—	0.0803	0.0595
n-Octane	126	0.1052	0.0920	0.0833	0.0786	0.0623

the specific retention volume of an adsorbate. This phenomenon is expected since the modified surfaces have less active sites available for surface interaction with an adsorbate and, therefore, the retention of a sorbate is decreased relative to its retention on unmodified silica gel. Elution peaks obtained were generally narrower and more symmetrical on modified columns than on unmodified columns; thus, salt modification of adsorbent surfaces improved the homogeneity of the adsorbent surface. Since samples were injected as the vapors from above the liquid in a vial, the measured retention times of sorbates were independent of sample size, which indicated that the chromatographic process was conducted on the linear region of the adsorption isotherm.

Examination of the data for the aromatics establishes that the V_s^T values decrease in the order of silica gel, 10% $MnCl_2$/silica gel, 10% $CoCl_2$/silica gel, 10% $ZnCl_2$/silica gel, 10% $CaCl_2$/silica gel. The same trend is exhibited for the saturated aliphatics studied; however, this trend is not followed by the olefinic sorbates. For example, the C_5 and the C_6 alkenes show a greater interaction on 10% $CoCl_2$/silica gel column, whereas the C_7 olefin is not eluted from both 10% $MnCl_2$/silica gel and 10% $CoCl_2$/silica gel.

Specific retention volumes and free energies of adsorption

Aromatic sorbates. The adsorption of a molecule on a sorbent surface can be considered as a reaction of the type

$$X(g) + A(s) \overset{K}{\rightleftharpoons} AX(s)$$
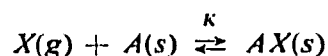
where $X(g)$ is the sorbate in the gas phase, $A(s)$ is the sorbent surface, $AX(s)$ is the adsorbed sorbate on the solid sorbent surface, and K is the distribution constant for the equilibrium. The specific retention volumes and the free energies of adsorption are proportional to the chemical potential. The free energy data presented in Table II indicate that the sorbate–sorbent interaction of aromatic sorbates on various columns

TABLE II

FREE ENERGIES OF ADSORPTION, $-\Delta G_a$, AT 235 °C (kcal/mole)

Compound	Silica gel	10% $MnCl_2$	10% $CoCl_2$	10% $ZnCl_2$	10% $CaCl_2$
Benzene	2.39	2.64	2.80	2.82	2.80
Fluorobenzene	2.49	2.63	2.77	2.80	2.80
Toluene	1.57	1.86	2.04	2.10	2.12
Chlorobenzene	1.77	1.88	2.07	2.10	2.13
Bromobenzene	1.32	1.49	1.62	1.67	1.71
Ethylbenzene	0.95	1.29	1.43	1.52	1.56
Cumene	0.45	0.82	0.94	1.05	1.18
Pentane	4.19	4.16	4.26	4.32	4.42
1-Pentene	1.89	3.62	3.41	3.71	3.93
n-Hexane	3.41	3.47	3.68	3.67	3.81
1-Hexene	—	3.04	2.87	3.03	3.38
n-Heptane	2.82	2.98	3.07	—	3.24
1-Heptene	—	—	—	2.54	2.83
n-Octane	2.86	2.40	2.50	2.55	2.79

increases in the following sequence: silica gel, $MnCl_2$, $CoCl_2$, $ZnCl_2$, $CaCl_2$. Although there may not be a significant difference in the values for the $CoCl_2$- and $ZnCl_2$-modified columns, the general trend prevails.

The forces responsible for the free energy of adsorption are of two kinds, *viz.* specific and nonspecific. The free energies computed in this study represent the total sorbent–sorbate interaction, *i.e.*

$$\Delta G = \Delta G_{specific} + \Delta G_{nonspecific}$$

Since, for a given sorbate, operating conditions were identical for all columns, the data imply that differences in free energies of adsorption must be due to differences in the modified sorbent. Consideration of several possible types of specific interaction yields some insight into the adsorption process. One type of interaction possible is complexation between the π-systems of the unsaturated sorbates and vacant orbitals of the salt. This type of interaction can be best described as a Lewis acid–base type of electron transfer reaction. It is interesting to note that within the salt series $MnCl_2$, $CoCl_2$, $ZnCl_2$, which have the electronic configuration of $3d^5$, $3d^7$, and $3d^{10}$, respectively, the degree of adsorption of sorbates on these columns follows the same order.

The specific retention volumes of two closely boiling pairs of compounds with different degrees of polarity are presented in Table III. If dipole–dipole interaction between sorbent and sorbate is the main contribution to the retention of polar compounds, then the more polar compounds within a group should be eluted last. However, chlorobenzene is eluted before ethylbenzene and bromobenzene before cumene on the $MnCl_2$-modified silica gel, both cases being in opposition to polarity considerations. A similar trend between the same sorbates exists on the other columns investigated. One possible explanation for the longer retention of alkyl-substituted aromatic hydrocarbons over the halogenated aromatics is the electron-withdrawing capability of the halogens and the resultant loss in electron density in the aryl ring. This would cause a decreased sorbate–sorbent interaction. Another factor may be the polarizability of the molecule, which is reflected by its molar refraction at 25 °C. As seen in Table III, there is a fair correlation between the specific retention volumes of sorbates and their corresponding molar refractions. Plots of log V_s^T *versus* molar refraction, such as illustrated by the example in Fig. 1, indicate that sorbate adsorption on these columns is a linear function of the polarizability of the sorbate.

TABLE III

EFFECT OF DIPOLE MOMENT AND MOLAR REFRACTION UPON RETENTION VOLUMES AT 250 °C ON 10% $MnCl_2$/SILICA GEL

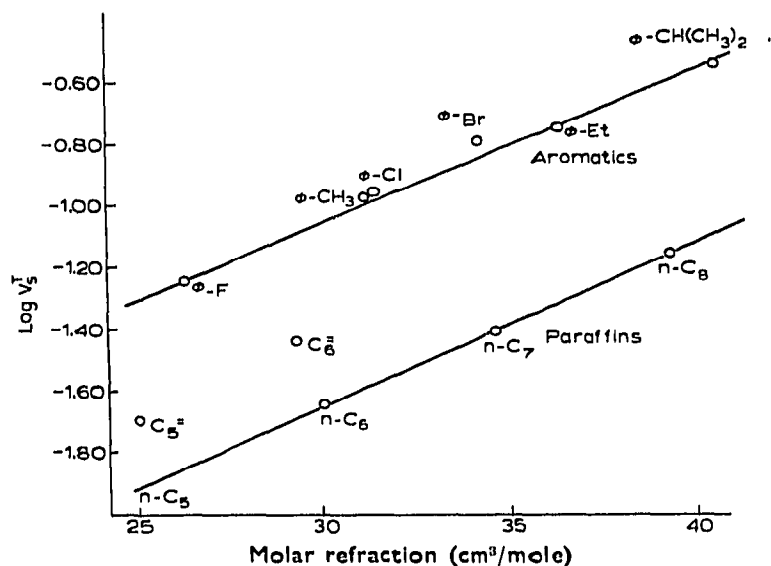| Pair of compounds	B.p. (°C)	V_s^T	Dipole moment	Molar refraction (cm³/mole)
A Ethylbenzene	132	0.1861	0.6	36.2
Chlorobenzene	136	0.1100	1.7	31.2
B Cumene	152	0.2921	0.8	40.5
Bromobenzene	155	0.1655	1.7	34.1

Fig. 1. Log $V_s^{250\ °C}$ versus molar refraction on 10% MnCl$_2$/silica gel.

Aliphatic sorbates. The adsorption of the saturated normal aliphatics exhibits the same trends from column to column as the aromatics (see Tables I and II). This implies that the trend of nonspecific interactions is the same as the nonspecific interactions of the aromatics on all the columns investigated. Inspection of the retention volumes of several closely boiling linear hydrocarbons appearing in Table I depicts the effect of π-electrons on sorbate retention. These compounds have been chosen on the assumption that their similarity in boiling points reflect a similarity in the degree of nonspecific adsorption. The data indicate that the retention is dependent on the degree of π-electron character of the sorbate. A similar trend was observed for the aromatic sorbates.

The plots of log V_s^T versus molar refraction indicate that polarization effects are also important with the olefins (Fig. 1). It is noted that the points for the olefins lie between the normal alkane line and the aromatic line, implying that the polarization effect on the olefins is less dominant than for the aromatic sorbates studies. It is also interesting to note that the observed trend of adsorption from column to column for the olefins is not the same as for the aromatics, as reflected by the V_s^T and ΔG values. Presumably, the interaction responsible for $\Delta G_{specific}$ for the olefins is of a different nature than for the aromatics. Alternatively, the main contribution to ΔG for the olefins may be one of the forces operating in aromatic adsorption but is enhanced with the olefins. It is not unreasonable that the olefins show a different adsorption trend because of the differences in π-electronic centers available, namely, the resonance which stabilizes the aromatic sorbates is not available for the olefins. The data in Tables I and II, in general, indicate that within the salt series MnCl$_2$, CoCl$_2$, and ZnCl$_2$ the adsorption decreases in the sequence CoCl$_2$, MnCl$_2$, ZnCl$_2$.

Since 1-heptene is not eluted from both $MnCl_2$ and $CoCl_2$ columns, irreversible chemisorption must play an important role in olefin adsorption.

In general, $CoCl_2$-modified silica gel shows the greatest interaction with the olefins and there is little difference between the $MnCl_2$- and $ZnCl_2$-modified columns, although olefin adsorption is slightly greater on the $MnCl_2$-modified column. A similar trend was observed by Grob and McGonigle[10], in studies on olefinic complexation on pure salt adsorbents. These workers interpreted this trend as due to the particularly stable state of the d^5-system[10]. In the present study the different trend observed for the olefins as compared to the aromatics is interpreted as due to an enhanced π-electronic complexation of the olefins with the unfilled d orbitals of the salt as compared to the aromatic sorbates.

Heats and entropy of adsorption

Aromatic sorbates. Tables IV and V contain the heats of adsorption and the entropies of adsorption, respectively, of aromatic sorbates on all columns studied. Comparison of sorbate heats of adsorption on the same column are valid but comparisons of the same sorbate on different columns are meaningless, since the values of the entropies of adsorption vary from one column to another.

TABLE IV

HEATS OF ADSORPTION, $-\Delta H_a$ (kcal/mole)

Compound	Silica gel	10% MnCl$_2$	10% CoCl$_2$	10% ZnCl$_2$	10% CaCl$_2$
Benzene	11.37	10.57	10.18	9.79	11.35
Fluorobenzene	10.97	10.19	9.37	9.78	11.75
Toluene	15.27	12.53	11.76	12.14	12.54
Chlorobenzene	11.75	11.36	10.58	10.97	10.96
Bromobenzene	12.74	12.54	11.36	11.37	11.75
Ethylbenzene	16.06	14.10	14.11	13.32	13.71
Cumene	—	15.28	14.50	14.50	14.89
n-Pentane	7.44	8.22	8.99	8.23	9.79
1-Pentene	23.50	11.37	11.33	11.75	10.16
n-Hexane	8.21	8.58	9.01	9.03	12.54
1-Hexene	—	10.58	14.11	11.35	11.73
n-Heptane	9.77	10.19	9.79	9.42	10.92
1-Heptene	—	—	—	12.53	11.35
n-Octane	10.95	11.37	10.57	10.98	10.95

Comparisons of the heats between sorbates of similar boiling points on the same column indicate the same trends as the values in Tables I and II. For example, in the $MnCl_2$-modified column, ethylbenzene and chlorobenzene have heats of adsorption values of 14.10 and 11.36 kcal/mole, respectively. These data are consistent with the observation that ethylbenzene is eluted after chlorobenzene. Similar comparisons between sorbates on other columns show the same trends.

Aliphatic sorbates. The effect of the π-character of the double bond can again be demonstrated when comparisons are made between a given olefin and its saturated analog. For example, on the $MnCl_2$-modified column, n-pentane and 1-pentene have

TABLE V
ENTROPIES OF ADSORPTION, $-\Delta S_a$, AT 250 °C (ENTROPY UNITS)

Compound	Silica gel	10% $MnCl_2$	10% $CoCl_2$	10% $ZnCl_2$	10% $CaCl_2$
Benzene	16.41	14.38	13.33	12.57	15.50
Fluorobenzene	—	13.77	11.88	12.56	16.25
Toluene	25.17	19.52	17.88	18.39	19.14
Chlorobenzene	18.34	17.34	15.55	16.20	16.08
Bromobenzene	21.05	20.40	17.86	17.82	18.43
Ethylbenzene	27.96	23.61	23.42	21.72	22.33
Cumene	—	26.76	25.04	24.87	25.35
n-Pentane	5.64	7.05	8.17	6.74	9.49
1-Pentene	39.86	14.00	14.11	14.54	10.96
n-Hexane	8.40	8.88	9.49	9.66	15.77
1-Hexene	—	13.68	20.59	15.05	14.99
n-Heptane	12.44	13.06	12.11	11.42	13.62
1-Heptene	—	—	—	18.26	15.38
n-Octane	15.78	16.41	14.69	15.43	14.78

heats of 8.22 and 11.37 kcal/mole, respectively, while n-hexane and 1-hexene have heats of 8.58 and 10.58 kcal/mole, respectively. The introduction of a double bond into a hydrocarbon significantly enhances the interaction on a salt-modified column. It is interesting to note the extremely large value of 23.50 kcal/mole associated with 1-pentene on the unmodified silica gel column. Certainly chemisorption plays a key role on the adsorption of olefins on silica gel. The values of ΔH for 1-hexene and 1-heptene on silica gel were not determined since these sorbates displayed extreme broadening and tailing of elution peaks with very long retention times.

CONCLUSIONS

Salt modification of silica gel surfaces has proved to be useful in producing a more homogeneous adsorbent with a decreased surface area. The modified adsorbents yield more symmetrical elution peaks with decreased retention times, which allows a faster analysis time and the computation of accurate thermodynamic data. Depending upon the nature of the modifying agent, different degrees of sorbate selectivity can be incorporated into adsorbents, thus extending the versatility of GSC.

Sorbate adsorption is determined by both specific and nonspecific sorbate–sorbent interactions. The adsorption of aromatics, olefins and saturated paraffins on the columns used in this investigation is primarily dependent on specific interactions caused by cation polarization effects and salt "d orbital" sorbate complexation. Olefinic sorbates show a greater orbital complexation than polarization interaction, while aromatic sorbates exhibit a greater polarization interaction.

ACKNOWLEDGEMENTS

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