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Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

The principles and Practice of GaS-Solid Chromatography With Salt-Modified Adsorbents

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To cite this Article Okamura, Judy P. and Sawyer, Donald T.(1973) 'The principles and Practice of GaS-Solid Chromatography With Salt-Modified Adsorbents', Separation & Purification Reviews, 1: 1, 409 — 475
To link to this Article: DOI: 10.1080/03602547308068945
URL: http://dx.doi.org/10.1080/03602547308068945

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SEPARATION AND PURIFICATION METHODS, 1(2), 409-475 (1972)

THE PRINCIPLES AND PRACTICE OF GAS-SOLID CHROMATOGRAPHY WITH SALT-MODIFIED ADSORBENTS

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INTRODUCTION

Although the concept and practice of gas-solid chromatography predates the first description of gas-liquid chromatography[1] in 1952 by several years, it has not enjoyed comparable popularity. The subject of gas-solid chromatography was a significant part of a Faraday Society meeting on chromatography in 1949.[2-4] However, the practical use of gas-solid chromatography through the 1950's was limited mainly to the separation of low-boiling gases whose separations were not easily accomplished by gas-liquid chromatography.[5]

In the mid-1960's interest in gas-solid chromatography was revived. The advent of the flame ionization detector and the work of Scott and Phillips[6-9] with salt-modified adsorbents illustrated that for sufficiently small sample sizes the partitioning process occurs on the linear portion of the adsorption isotherm, and thereby gives symmetrical elution peaks. It had long been recognized that if the problem of nonsymmetrical peaks could be overcome several advantages of gas-solid chromatography could be realized. These include a) higher column efficiencies because of the absence of a

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liquid-phase contribution to band-spreading; b) high column temperature limits; c) stable surfaces which do not undergo oxidation or other chemical reactions; d) selective separations; and e) absence of the "bleeding" problem that occurs with liquid phases to cause contamination and background noise for the more sensitive detectors.

Figure 1 illustrates the importance of a sensitive detector in gas-solid chromatography.[7] The larger sample sizes required by the katharometer detector lie on the non-linear region of the adsorption isotherm and result in skewed peak shapes, while the smaller sample sizes required by the argon detector lie on the linear region and give good gaussian peak shapes.

In addition to extending the linear isotherm region for solid adsorbents, salt modification allows a large variety of adsorbents to be prepared by the use of

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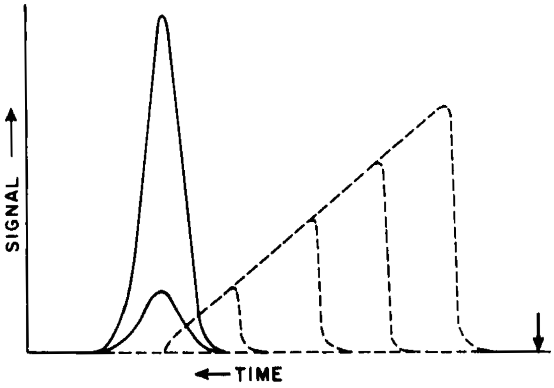

FIGURE 1

Peak shapes for elution of cyclohexane from alumina modified with NaOH, at 291 °K. Sample sizes consistent with sensitivity of argon detector (——) and katharometer detector (-----).

different modifying salts. Changing the modifier salt often results in large changes in the separation characteristics of an adsorbent. Figure 2 illustrates an early study done by Scott and Phillips[8] which used 14 alkali metal salts (halides and hydroxides) on silica-alumina. The "Kovat" retention indices for the retention of benzene on the unmodified base and the different salt-modified columns are given. Note that the retention of benzene can range anywhere from heptane to undecane. The use of these similar salts only begins to illustrate the potential in selective separations which can be achieved by salt-modified gas-solid chromatography.

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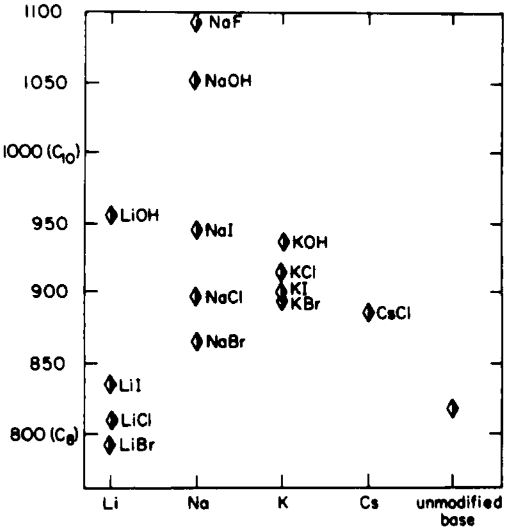

FIGURE 2

Kovat retention indices (ordinate) for benzene with respect to various modifiers on silica-alumina. Column temperature 150 °C. Index values for *n*-octane and *n*-decane indicated on ordinate.

TECHNIQUE OF SALT-MODIFIED GAS-SOLID CHROMATOGRAPHY

A basic question in the use of salt-modified adsorbents is what are the effects of the amount and the kind of coating salt upon the retention of sorbate molecules. The answer to this question has been approached in terms of the kinds of adsorption processes.[10]

Two types of interactions can occur between adsorbate molecules and the ionic surfaces of the adsorbents that are produced by the modification procedure. The first of these is due to dispersion forces and can be termed a nonspecific interaction.[11] Adsorbates possessing either spherically symmetrical electron shells or sigma bonds interact with the adsorbent by this process. The second type of interaction involves adsorbate molecules having isolated sites, individual bonds, or a system of bonds of high electron density. Molecules with pi-electron systems, lone electron pairs, and related functional groups can interact specifically with the ionic surface.[12]

The variation of the energetics for nonspecific interactions with percent modification can be evaluated by measuring the specific retention volume ($\underline{V}_{\underline{s}}^{T}$) for a molecule which is subject only to such interactions. To determine functional dependence of specific interaction energies on surface modification is more difficult because any test molecule which interacts with a surface also interacts nonspecifically. However, this functional dependence can be determined by comparing the behavior of two molecules which are similar in structure and physical properties such that they have the same nonspecific interactions with the surface. If one of the molecules also is subject to specific interactions, then the difference in retention for the two

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molecules is a measure of these specific effects. Figure 3 illustrates the variation of both types of interactions with loading for Na_2SO_4 and Na_3PO_4 at a column temperature of 100°C. The lower set of curves, which represent the logarithm of the specific retention volume of pentane as a function of the amount of coating, illustrates the dependence of nonspecific interactions

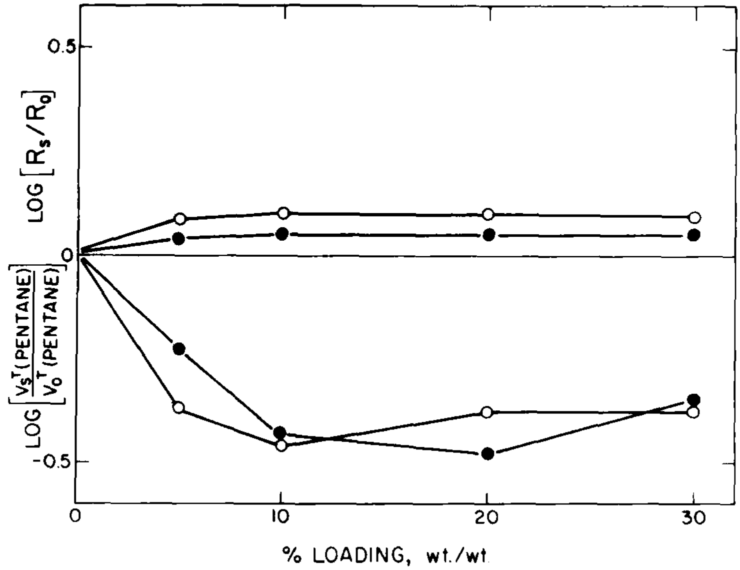

FIGURE 3

Effect of surface coating on nonspecific (lower curves) and specific (upper curves) interactions.

●, Na_2SO_4; O, Na_3PO_4. Specific retention volumes for uncoated alumina; $\underline{V}^T_{\underline{s}_{\underline{o}}}$(pentane), 0.26 ml/meter^2; $\underline{V}^T_{\underline{s}_{\underline{o}}}$(pentene-1), 0.56 ml/meter^2. log [$\underline{R}_{\underline{s}}/\underline{R}_{\underline{o}}$] = log [$\underline{V}^T_{\underline{s}}$(pentene-1/$\underline{V}^T_{\underline{s}}$(pentane)] - log [$\underline{V}^T_{\underline{s}_{\underline{o}}}$(pentene-1/ $\underline{V}^T_{\underline{s}_{\underline{o}}}$(pentane)].

on the degree of modification. The upper curves present the values of $\log[V_s^T(\text{pentene-1})/V_s^T(\text{pentane})] - \log[V_{s_o}^T(\text{pentene-1})/V_{s_o}^T(\text{pentane})]$ as a function of the amount of loading; $V_{s_o}^T$ represents the specific retention volume on uncoated alumina. The data indicate the variation of specific interaction energies with degree of modification relative to those for a column with zero loading. The assumption has been made that the logarithmic terms are functions only of the specific interaction of a pi bond with the surface, *i.e.*, that the nonspecific interactions of pentene-1 and pentane with the surface are the same and cancel in the expression. Figure 3 indicates that both specific and nonspecific interactions become essentially independent of amount of coating above 10% by weight. The relative change with amount of coating for the nonspecific inter-actions is much greater than that for the specific interactions. Thus, surface modification appears to block the high energy nonspecific sites (such as capillaries) rather than to alter the energetics of the specific sites on the surface.

The nature of the specific interactions is illustrated by some of the selective separations which have been achieved.[12] Comparison of compounds with similar structures allows isolation and evaluation of specific molecular features which influence retention.

The retention volumes of several closely boiling groups of compounds with different degrees of polarity are listed in Table I. If dipole-dipole interaction between the adsorbent and the adsorbate were the main contribution to retention of polar compounds, then the more polar compound within the groups should be eluted

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TABLE I

Effect of Dipole Moment upon Retention Volumes
for Compounds of Similar Boiling Point
Column: F-1 alumina coated with 10% NaCl, 250° C

	Compound	Boiling point, °C	Dipole moment, Debye	$\underline{V_R}$, ml	Molar refraction cm^3/mol
A.	Ethylbenzene	132	0.6	52.8	36.2
	Chlorobenzene	136	1.7	38.8	31.2
B.	Cumene	152	0.8	72.1	40.5
	Bromobenzene	155	1.7	59.4	34.1
C.	o-Chlorotoluene	159	1.9	79.5	35.8
	m-Chlorotoluene	161	1.8	72.4	36.2
	p-Chlorotoluene	159	1.9	79.5	36.2

last. However, chlorobenzene is eluted before ethylbenzene and bromobenzene is eluted before cumene, both cases being in opposition to polarity considerations. A possible explanation for the longer retention of the alkyl-substituted aromatic hydrocarbons over the halobenzenes is the electron withdrawing propensity shown by the halogen and the concomitant loss in electron density in the aryl ring. This would cause a decreased interaction between the adsorbate and adsorbent and be reflected by decreased retention volumes. Another factor may be the polarizability of the molecules which is indicated by their molar refraction. Values of the latter are tabulated in Table I and, within the first two groups, give a fair correlation with retention volume. In contrast, the retention volumes of the chlorotoluenes follow closely the order of their polarity (Table I). The difference between the aryl halides and the chloro-

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toluenes can be rationalized on the basis that each isomer of the latter has approximately the same ring electron density (neglecting, as a first approximation, the effect of differing position of ring substitution), because each has identical substituents. Hence, only polarity differences contribute to their relative retention.

The retention volumes of several closely-boiling linear and cyclic six-carbon hydrocarbons are tabulated in Table II, and indicate the effect of pi-electrons and structure on retention. These compounds have been chosen on the assumption that their similarity in boiling point reflects a similarity in degree of nonspecific adsorption.

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TABLE II

Effect of Pi Electrons and Structure upon Retention Volumes for Compounds of Similar Boiling Point

Column: F-1 alumina coated with 10% NaCl, 250° C

	Compound	Boiling point, °C	$\underline{V}_R$, ml
A.	Hexane	69	7.89
	Hexene-1	63.5	10.2
	cis-Hexene-2	69	10.4
	trans-Hexene-2	68	9.20
	1,4-Hexadiene	65	11.5
B.	Cyclohexane	81	7.78
	Cyclohexene	83	10.5
	1,3-Cyclohexadiene	80.5	14.0
	1,4-Cyclohexadiene	86.5	15.4
	Benzene	80	17.0

PRINCIPLES OF SELECTIVE AND SPECIFIC INTERACTIONS

Because most gas chromatographic studies are reported at only one temperature, predictions of the separation that will be achieved at some other temperature are difficult. For this reason the study of salt-modified gas-solid chromatography has been approached in terms of the thermodynamics of adsorption. The enthalpies and entropies of adsorption thus obtained can be used to predict retention volumes and separations at any temperature. An early study established that the enthalpies and entropies of adsorption are combinations of nonspecific and specific contributions.[10]

The overall interaction between sorbate and adsorbent is dependent on the nature of the coating salt and the coated substrate. Hence, alterations of both salt and substrate provide a means for developing selectivity for a given sample mixture.

Adsorption Thermodynamics.[13] For elution gas-solid chromatography, the corrected retention volume, $\underline{V_R}$ can be converted to the specific retention volume, $\underline{V_S^T}$, by dividing by the surface area of the adsorbent, A. The corrected specific retention volume at the column temperature for a given sorbate-sorbent pair is equal to the distribution constant, $\underline{K}$,

$$V_R/A = V_s^T = K = C_{(s)}/C_{(g)}\ (\mathrm{ml/m^2}) \qquad (1a)$$

where $\underline{K}$ is the ratio of the equilibrium surface concentration to the gas phase concentration of the sorbate with the surface concentration expressed as moles per square meter and the gas phase concentration as moles per milliliter. If the surface concentration is expressed as moles per square centimeter, then the distribution constant is given as $\underline{K}'$

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$$K'(\mathrm{ml/cm^2}) = 10^{-4}K(\mathrm{ml/m^2}) \qquad (1b)$$

The free energy of adsorption is related to the distribution constant by the relation

$$-\Delta G'_{ads} = RT \ln K = RT \ln V_s^T = -\Delta H'_{ads} + T\Delta S'_{ads} \qquad (2)$$

which can be rearranged to give the specific retention volume as a function of the enthalpy and entropy of adsorption

$$\log V_s^T = -\Delta G'_{ads}/2.3RT = -\Delta H'_{ads}/2.3RT + \Delta S_{ads}/2.3R \quad (3)$$

By assuming idealized standard states the standard state free energies and entropies of adsorption ($\Delta \underline{G}^o_{\underline{ads}}$ and $\Delta \underline{S}^o_{\underline{ads}}$) can be determined from the gas chromatographic retention data. For the gas phase, the standard state of the adsorbate is defined as a partial pressure of one atmosphere with the adsorbate vapor behaving as a perfect gas. The standard state for the adsorbed phase is that suggested by de Boer and Kruyer;[14] namely, a two-dimensional perfect gas at one atmosphere. Hence, the mean distance between adsorbed molecules is defined to be the same as in the three-dimensional gas phase standard state. Thus, by solving for the intermolecular distance, the area per molecule can be evaluated at standard conditions. This leads to a standard state surface concentration, $\underline{C}^o_{(\underline{s})}$, which is given by the expression

$$C^o_{(s)} = 4.07 \times 10^{-9}/T(\mathrm{moles/cm^2}) \qquad (4)$$

at the column temperature, $\underline{T}$. Combining Equation 1 and Equation 4 gives the gas phase sorbate concentration, $\underline{C}_{(\underline{g})}$,

$$C_{(g)} = 4.07 \times 10^{-9}/TK' \qquad (5)$$

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which, when combined with the perfect gas equation, gives

$$P_{(equil)} = C_{(g)}RT = 4.07 \times 10^{-9}R/K' \quad (6)$$

Knowing the equilibrium partial pressure, $\underline{P}_{(equil)}$, of sorbate vapor in equilibrium with the sorbent permits evaluation of the differential molar free energy, $\underline{\Delta G}^{o}$, for transfer of one mole of vapor at one atmosphere to its equilibrium vapor pressure, $\underline{P}_{(equil)}$.

$$\Delta G^{o} = RT \ln[P_{(equil)}/1] = RT \ln[4.07 \times 10^{-9}R/K'] \quad (7a)$$

Substitution of Equation 1b into Equation 7a gives

$$\Delta G^{o} = RT \ln[4.07 \times 10^{-5}R/K] = RT \ln[4.07 \times 10^{-5}R/V_s^{T}] \quad (7b)$$

Substitution of constants and combining of terms gives

$$\begin{aligned} \Delta G^{o} &= RT \ln(4.07 \times 10^{-5} \times 82.05) - RT \ln V_s^{T} \\ &= 1.99T \ln(4.07 \times 10^{-5} \times 82.05 + \Delta G_{ads} \\ &= \Delta G'_{ads} - 11.33T \end{aligned} \quad (7c)$$

Further rearrangement gives a relation between the specific retention volume and the free energy of adsorption as a function of temperature,

$$\log V_s^{T} = [-\Delta G^{o}_{ads}/4.58] - 2.48 = -\Delta G'_{ads}/4.58T \quad (7d)$$

with the specific retention volume, $\underline{V_s^{T}}$, in ml/meter^2 and the free energy, $\underline{\Delta G'_{ads}}$, in calories.

A thermodynamically based retention index has been developed by determining the entropies and enthalpies of adsorption for various functional groups.[13,15-19] To accomplish this the logarithm of the specific retention volume of a compound has been divided into additive components

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$$\log V_s^T = (\log V_s^T)_o + n(\log V_s^T)_C + m(\log V_s^T)_\pi + (\log V_s^T)_{\varphi\ \mathrm{subst}} \qquad (8)$$

with $(\log \underline{V_s}^T)_o$ the zero point value, $(\log \underline{V_s}^T)_{\underline{C}}$ the contribution per carbon atom, $\underline{n}$ the number of carbon atoms, $(\log \underline{V_s}^T)_\pi$ the contribution per π bond, $\underline{m}$ the number of π bonds, and $(\log \underline{V_s}^T)_{\varphi\text{-}\underline{\mathrm{subst}}}$ the contribution of a substituent attached to a benzene ring.

The method of obtaining such data has been to first plot $\underline{V_s}^T$ versus carbon number for a series of normal alkanes. The slope of the plot gives $(\log \underline{V_s}^T)_{\underline{C}}$, the contribution per carbon (really per $-CH_2-$ group), and the intercept gives the zero point $(\log \underline{V_s}^T)$ value. The $(\log \underline{V_s}^T)_\pi$ term has been obtained from the difference in log $\underline{V_s}^T$ units between an alkene and an alkane with the same number of carbon atoms. The data for aryl substituents result from the differences in log $\underline{V_s}^T$ units between benzene and the substituted benzenes. These functional group terms have been evaluated at three different temperatures and analyzed by Equation 3 to obtain the enthalpy and entropy of adsorption for each functional group. An example[20] of how the contributions are evaluated at one temperature is illustrated by Figure 4. The resulting contributions and their differential enthalpies and entropies are summarized in Table III.[13]

The development of porous glass beads with controlled pore sizes and surface areas has provided a valuable new support for salt-modified gas-solid chromatography. This type of support has been selected to study the effect that different salts have on the thermodynam-

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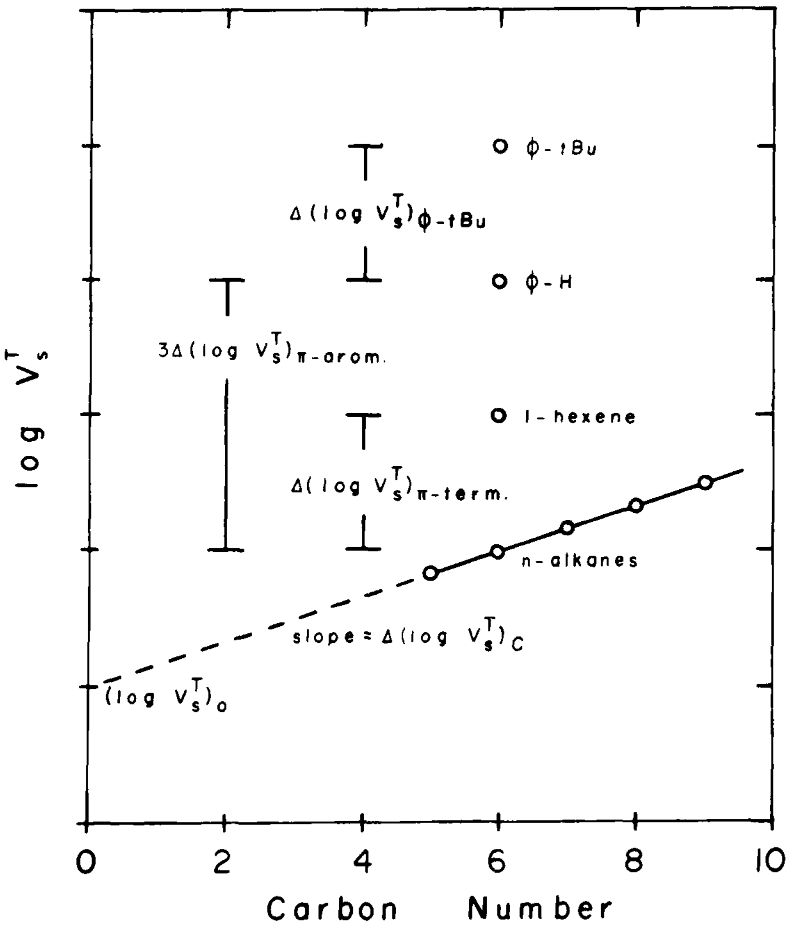

FIGURE 4

Evaluation of adsorptive contributions from a log $\underline{V_s^T}$ $\underline{\text{vs}}$. carbon number plot.

ics of adsorption of specific interactions.[19] Of the various forms of porous beads available, Porasil C (Waters Associates, Framingham, Mass.) has been used because its surface area offers a compromise in selectivity, operating temperature, and analysis time.

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TABLE III

Retention Volume Indices and Thermodynamic Parameters for Various Functional Groups on 10% Na_2SO_4 Modified Acid-Washed F-1 Alumina

x	$(\log \underline{V}_s^T)_x$ 200°	$(\log \underline{V}_s^T)_x$ 225°	$(\log \underline{V}_s^T)_x$ 250°	$\Delta(-\Delta\underline{H}')_x$	$\Delta(-\Delta\underline{S}')_x$	500° $\Delta(-\Delta\underline{G}')_x$
o	-3.358	-3.518	-3.483	-0.30	15.61	-8.10
C	0.298	0.268	0.239	1.33	1.44	0.61
π_{term}	0.233	0.206	0.175	1.32	1.71	0.46
π_{trans}	0.182	0.149	0.125	1.31	1.95	0.33
π_{cis}	0.274	0.229	0.193	1.85	2.66	0.52
π_{conj}	0.367	0.307	0.262	2.38	3.38	0.69
π_{arom}	0.260	0.232	0.206	1.31	1.57	0.52
φ-CH_3	0.341	0.301	0.266	1.70	2.04	0.68
-Et	0.628	0.540	0.483	3.28	4.11	1.22
-iPr	0.747	0.649	0.583	3.73	4.52	1.47
-tBu	0.942	0.824	0.741	4.56	5.38	1.87
-CF_3	--	--	--	--	--	--
-F	0.081	0.059	0.054	0.60	0.94	0.13
-Cl	0.394	0.338	0.298	2.17	2.81	0.75
-Br	0.634	0.555	0.598	3.09	3.66	1.26
-I	--	0.835	0.751	4.00	4.22	1.89
-OCH_3	--	--	--	--	--	--

$$\log \underline{V}_s^{500} \quad \Sigma(-\Delta\underline{G}')_x/2.29$$

Consideration of the data in Tables IV and V establishes that the inorganic salts used for salt-coating Porasil C have a significant effect on the various specific interactions. Although Na_2SO_4, NaCl, and LiBr act similarly at 500 ^oK, differences in enthalpies and entropies exist as indicated by Table VI.

Na_3PO_4 and Na_2MoO_4 are similar to the other Group I salts with the exception that π interactions are enhanced slightly with Na_2MoO_4 and even more with Na_3PO_4. The nature of the anionic portion of the salt does not seem to have a major effect on its adsorptive properties.

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Both $CoSO_4$ and $NiSO_4$ behave similarly, but the properties of 10% $NiSO_4$ on Porasil C change with time such that the column is impractical and comparisons are meaningless. The C_H and φ-Alk free energy contributions for $CoSO_4$ at 500 ^oK are enhanced compared with Group I salts. Although olefinic compounds are not eluted from $CoSO_4$ modified Porasil C, the $\pi_{\underline{aromatic}}$ free energy contribution at 500 ^oK is comparable to that on Na_3PO_4. However, the enthalpy and entropy contributions for $\pi_{\underline{aromatic}}$ electrons are much greater on $CoSO_4$. The change in thermodynamic parameters per halogen is greater on $CoSO_4$ than on Group I salts.

When $Al_2(SO_4)_3$ and $Cr(SO_4)_3$ are used as coating salts, olefinic compounds are not eluted from either column. Alkyl-substituted benzenes are not eluted from $Cr_2(SO_4)_3$, but with $Al_2(SO_4)_3$ they interact similarly to Group I salts except that t-butylbenzene is not eluted. The C_H free energy contribution at 500 ^oK is similar on $Al_2(SO_4)_3$ and Group I salts, but is the largest of any salt examined on $Cr_2(SO_4)_3$. The φ-X free energy contri-

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TABLE IV

Effect of Coating Salt (10% wt/wt) on Porasil C
on Thermodynamic Parameters for Various Functional Groups
(Enthalpies in Kilocalories; Entropies in Entropy Units)

	NaCl		LiBr		Na_3PO_4		Na_2MoO_4	
x	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$
o	2.25	19.57	3.37	21.74	2.91	20.81	1.66	18.24
C	0.74	0.69	0.60	0.42	0.69	0.60	0.87	0.92
π_{term}	1.10	1.56	0.82	1.07	1.42	2.15	1.08	1.48
$\pi_{cis-trans}$	1.71	2.77	1.21	1.78	1.55	2.32	1.19	1.67
π_{conj}	1.69	2.56	1.38	1.98	1.85	2.73	1.73	2.57
π_{arom}	1.26	1.88	0.77	0.97	1.31	1.84	1.18	1.71
ω-CH_3	1.84	2.70	1.82	2.61	1.55	2.09	1.85	2.60
-Et	2.76	3.72	2.58	3.38	2.46	3.05	2.96	3.99
-iPr	3.37	4.42	3.20	4.11	3.03	3.70	3.63	4.78
-tBu	4.23	5.57	3.99	5.10	3.77	4.59	4.48	5.83
-CF_3	-0.96	-2.27	--	--	-0.80	-1.97	-0.25	-0.91
-F	-1.35	-2.58	-0.46	-0.98	-0.67	-1.23	-0.69	-1.30
-Cl	-0.69	-2.13	0.04	-0.74	-0.47	-1.63	-0.22	-1.25
-Br	-0.10	-1.52	0.59	-0.18	0.01	-1.27	0.54	-0.33
-I	0.67	-0.68	1.19	0.29	0.52	-1.05	1.55	0.82
-OCH_3	5.88	7.76	8.17	11.01	5.95	7.51	6.18	8.16

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TABLE IV, continued:

	$COSO_4$		$Al_2(SO_4)_3$		$Cr_2(SO_4)_3$	
x	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$
o	1.39	17.90	1.43	17.93	-1.42	12.69
C	0.98	1.11	0.92	1.06	1.60	2.21
π_{term}	--	--	--	--	--	--
$\pi_{cis-trans}$	--	--	--	--	--	--
π_{conj}	--	--	--	--	--	--
π_{arom}	1.93	3.14	0.68	0.86	-0.89	1.21
φ-CH_3	3.60	4.68	2.05	3.09	--	--
-Et	4.70	6.04	2.84	3.87	--	--
-iPr	5.34	6.64	3.87	5.39	--	--
-tBu	6.00	7.04	--	--	--	--
-CF_3	--	--	--	--	--	--
-F	-3.60	-6.67	-0.26	-0.65	-0.28	-0.51
-Cl	0.22	-0.19	0.73	0.46	1.74	2.26
-Br	1.13	0.69	1.56	1.51	3.07	4.13
-I	4.51	6.19	2.47	2.54	4.92	6.74
-OCH_3	--	--	--	--	--	--

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TABLE V

Effect of Coating Salt (10% wt/wt) on Porasil C on Free Energies of Adsorption for Various Functional Groups $[\Delta(-\Delta\underline{G})_x$, 500 ^{o}K, in Kilocalories]

x	NaCl	LiBr	Na_3PO_4	Na_2MoO_4	$CoSO_4$	$Al_2(SO_4)_3$	$Cr_2(SO_4)_3$
o	-7.53	-7.50	-7.49	-7.45	-7.55	-7.53	-7.77
C	0.39	0.39	0.39	0.41	0.42	0.39	0.50
π_{term}	0.32	0.29	0.35	0.33	--	--	--
$\pi_{cis\text{-}trans}$	0.33	0.31	0.39	0.36	--	--	--
π_{conj}	0.41	0.39	0.48	0.44	--	--	--
π_{arom}	0.31	0.28	0.38	0.33	0.36	0.25	0.28
φ-CH_3	0.49	0.51	0.51	0.55	1.25	0.50	--
-Et	0.90	0.89	0.93	0.96	1.67	0.90	--
-iPr	1.16	1.14	1.18	1.24	2.02	1.17	--
-tBu	1.45	1.44	1.47	1.57	2.47	--	--
-CF_3	0.16	--	0.18	0.20	--	--	--
-F	-0.05	0.02	-0.06	-0.03	-0.27	0.06	-0.02
-Cl	0.37	0.41	0.34	0.40	0.32	0.50	0.61
-Br	0.65	0.69	0.65	0.71	0.78	0.80	1.00
-I	1.01	1.05	1.05	1.13	1.41	1.20	1.55
-OCH_3	1.99	2.66	2.19	2.09	--	--	--

TABLE VI

Comparison of Coating Salts on Enthalpies and Entropies of Adsorption

Contribution	Magnitude of $\Delta(-\Delta\underline{H})$ and $\Delta(-\Delta\underline{S})$
C_H	LiBr < NaCl < Na_2SO_4
π_{term}	LiBr < NaCl = Na_2SO_4
$\pi_{cis-trans}$	Na_2SO_4 < LiBr < NaCl
π_{conj}	Na_2SO_4 < LiBr < NaCl
π_{arom}	LiBr < Na_2SO_4 < NaCl
φ-Alk	Na_2SO_4 = NaCl = LiBr
φ-X	NaCl < Na_2SO_4 < LiBr
φ-OMe	Na_2SO_4 < NaCl < LiBr

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bution is enhanced when $Cr_2(SO_4)_3$ and $Al_2(SO_4)_3$ are used for coating; the φ-Cl, φ-Br, and φ-I enthalpy and entropy contributions on $Cr_2(SO_4)_3$ are the largest of any salt studied.

In general, free energy contributions are increased by decreasing the column temperature. However, because of negative entropy contributions, φ-F behaves in an opposite manner in all cases examined. The entropy contributions are negative for φ-Cl with all but the trivalent salts and for φ-Br with Group I salts only; φ-I has negative entropies on NaCl and Na_3PO_4. Compared with enthalpy contributions (kcal), φ-X entropy contributions (cal/deg) are smaller on all salts except for φ-I on $CoSO_4$, $Al_2(SO_4)_3$, and $Cr_2(SO_4)_3$ and for φ-Cl and φ-Br on $Cr_2(SO_4)_3$. For most other functional groups the entropy contribution is larger than the enthalpy contributions; for C_H both contributions are similar in magnitude.

The physical characteristics of the various unmodified and modified Porasils are summarized in Table VII.

The effect of surface area on the adsorptive thermodynamic parameters has been determined by use of a series of Porasils modified with a 10% (by weight) Na_2SO_4 coating; the results are summarized in Tables VIII and IX (data for Porasil C are included in Tables X and XI and are similar to Porasil D). In general, interactions increase with surface area. However, at 500 °K the free energy contributions for Porasil E are greater than those for Porasil D. For the halogenated

TABLE VII

Physical Characteristics of Various Modified and Unmodified Porous Silica Beads, 100-150 Mesh

Column Packing	Specific surface area, m²/g	Av. pore diam., Å	Operating temp., °C
Uncoated Porasil C	53	200-400	175-225
Silizaned Porasil C	62	200-400	125-175
Silizaned 10% Na_2SO_4-Porasil C	54	200-400	125-175
10% Na_2SO_4-Porasil A	455	100	200-250
10% Na_2SO_4-Porasil C	61	200-400	175-225
10% Na_2SO_4-Porasil D	33	400-800	150-200
10% Na_2SO_4-Porasil E	19	800-1500	125-175
10% NaCl-Porasil C	63	200-400	175-225
10% Na_2MoO_4-Porasil C	60	200-400	175-225
10% Na_3PO_4-Porasil C	57	200-400	175-225
10%LiBr-Porasil C	62	200-400	175-225
10% $NiSO_4$-Porasil C	82	200-400	175-225
10% $CoSO_4$-Porasil C	70	200-400	175-225
10% $Al_2(SO_4)_3$-Porasil C	68	200-400	175-225
10% $Cr_2(SO_4)_3$-Porasil C	67	200-400	175-225

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benzenes (φ-X) the free energy contributions are almost identical on Porasil C and D at 500 °K; the smaller entropy contributions on Porasil D cause larger free energy contributions at higher temperatures. For pi electron systems (π), the entropy contributions are much larger on Porasil A and D than on Porasil C and E.

The selectivity of a salt-modified adsorbent is strongly dependent upon the support that is to be modi-

TABLE VIII

Effects of Surface Area of 10% Na_2SO_4-Modified Porous Silica Beads on Free Energies of Adsorption for Various Functional Groups

[$\Delta(-\Delta\underline{G})_x$, 500 °K, in Kilocalories]

x	Porasil A	Porasil D	Porasil E
o	-7.63	-7.16	-7.64
C	0.42	0.35	0.41
π_{term}	0.44	0.25	0.34
$\pi_{cis-trans}$	0.45	0.26	0.33
π_{conj}	0.53	0.39	0.42
π_{arom}	0.38	0.31	0.32
φ-CH_3	0.57	0.46	0.44
-Et	1.07	0.84	0.83
-iPr	1.40	1.08	1.06
-tBu	1.78	1.37	1.34
-CF_3	-	0.18	0.26
-F	-0.05	-0.01	0.03
-Cl	0.48	0.38	0.46
-Br	0.85	0.67	0.75
-I	1.33	1.01	1.11
-OCH_3	-	-	2.00

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fied. Comparisons have been made of several adsorbents[13,16] that have been coated with Na_2SO_4; these include Florisil, Porasil, and F-1 Alumina (acid-washed and non-acid-washed).

Detailed consideration of the data in Tables X and XI indicates several interesting points. For example, with the Porasil C column the carbon of methyl substi-

TABLE IX

Effects of Surface Area of 10% Na_2SO_4-Modified Porous Silica Beads on Thermodynamic Parameters for Various Functional Groups

(Enthalpies in Kilocalories; Entropies in Entropy Units)

	Porasil A		Porasil D		Porasil E	
x	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$
o	-0.31	14.62	2.41	19.17	3.27	21.84
C	1.22	1.60	0.81	0.92	0.74	0.66
π_{term}	1.64	2.40	1.45	2.39	1.39	2.08
$\pi_{cis\text{-}trans}$	2.07	3.23	1.90	3.26	1.75	2.82
π_{conj}	2.03	3.00	1.84	2.90	1.85	2.85
π_{arom}	1.22	1.67	1.37	2.12	1.25	1.86
φ-CH_3	1.99	2.82	1.86	2.80	1.75	2.62
-Et	3.45	4.75	2.97	4.26	2.90	4.13
-iPr	4.33	5.85	3.61	5.05	3.67	5.21
-tBu	5.26	6.95	4.30	5.98	4.61	6.54
-CF_3	-	-	-0.83	-2.03	-0.40	-1.33
-F	-0.56	-1.00	-1.39	-2.75	-0.84	-1.76
-Cl	0.73	0.49	-0.81	-2.40	-0.09	-1.12
-Br	1.66	1.62	-0.19	-1.73	0.71	-0.08
-I	2.86	3.05	0.64	-0.74	1.69	1.15
-OCH_3	-	-	-	-	6.25	8.51

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TABLE X

Thermodynamic Parameters for Various Functional Groups on Four Different Adsorbents (Enthalpies in Kilocalories; Entropies in Entropy Units)

	10% Na_2SO_4- naw F-1 Al_2O_3		10% Na_2SO_4- aw F-1 Al_2O_3		10% Na_2SO_4- Porasil C		10% Na_2SO_4 Florisil	
x	$\Delta(-\Delta\underline{H}')_x$	$\Delta(-\Delta\underline{S}')_x$	$\Delta(-\Delta\underline{H}')_x$	$\Delta(-\Delta\underline{S}')_x$	$\Delta(-\Delta\underline{H}')_x$	$\Delta(-\Delta\underline{S}')_x$	$\Delta(-\Delta\underline{H})_x$	$\Delta(-\Delta\underline{S})_x$
o	-0.23	14.98	-0.30	15.61	1.33	16.69	1.61	12.69
C	1.34	1.46	1.33	1.44	0.86	0.97	1.59	1.67
π_{term}	1.10	1.43	1.32	1.71	1.02	1.52	1.67	2.32
π_{trans}	1.06	1.61	1.31	1.95	0.92	1.01	1.87	2.71
π_{cis}	1.34	1.86	1.85	2.66	0.92	1.01	1.87	2.71
π_{conj}	1.61	2.34	2.38	3.38	1.26	1.72	-	-
π_{arom}	1.35	2.00	1.31	1.57	1.11	1.69	1.23	1.52
φ-CH_3	1.40	1.57	1.70	2.04	1.83	2.59	2.68	3.02
-Et	2.63	2.85	3.28	4.11	2.77	3.69	4.29	4.76
-iPr	2.90	2.64	3.73	4.52	3.44	4.46	5.24	5.73
-tBu	4.46	4.83	4.56	5.38	4.20	5.35	-	-
-CF_3	1.85	2.06	-	-	-0.81	-2.17		
-F	1.00	1.25	0.60	0.94	-0.90	-1.70	0.16	0.08
-Cl	2.17	2.47	2.17	2.81	-0.49	-1.74	0.42	-0.41
-Br	3.00	3.26	3.09	3.66	0.22	-0.87	1.35	0.48
-I	4.12	4.28	4.00	4.22	1.01	0.08	2.55	1.63
-OCH_3	-	-	-	-	4.82	5.30		

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tuents on aromatic molecules has a larger interaction than that observed for an aliphatic carbon. A similar selectivity is not observed for the Na_2SO_4-alumina carbon. Another surprising observation is the small interaction of the fluorine substituent with a Na_2SO_4-Porasil C column relative to the Na_2SO_4-alumina column. The small interaction of aliphatic carbons on the Porasil C column relative to the alumina column pro-

TABLE XI

Specific Free Energy of Adsorption for Various Functional Groups, $\Delta(-\Delta \underline{G}')_x$, at 500 ^{o}K

x	10% Na_2SO_4- naw F-1 Al_2O_3	10% Na_2SO_4- aw F-1 Al_2O_3	10% Na_2SO_4- Porasil C	10% Na_2SO_4- Florisil
o	-7.72	-8.10	-7.01	-7.96
C	0.61	0.61	0.38	0.76
π_{term}	0.38	0.46	0.26	0.51
π_{trans}	0.25	0.33	0.41	0.51
π_{cis}	0.41	0.52	0.41	0.51
π_{conj}	0.44	0.69	0.40	-
π_{arom}	0.35	0.52	0.26	0.47
φ-CH_3	0.61	0.68	0.53	1.17
-Et	1.20	1.22	0.92	1.90
-iPr	1.58	1.47	1.21	2.37
-tBu	2.02	1.87	1.53	-
-CF_3	0.82	-	0.29	-
-F	0.37	0.13	-0.04	0.12
-Cl	0.93	0.75	0.39	0.63
-Br	1.37	1.26	0.66	1.11
-I	1.98	1.89	1.01	1.74
-OCH_3	-	-	2.03	-

vides an enhancement of the specific effects due to pi-bond interactions and allows more selective resolution of such specific interacting sorbates. In view of this enhancement, the inability to resolve <u>cis-trans</u> isomers on the Na_2SO_4-Porasil C column is surprising. This may be due to the particular pore size distribution of this material, or it may be due to specific surface effects that are different between silica and alumina.

An important observation is the effect that results from acid washing the alumina prior to coating it with the inorganic salt. Such treatment does not significantly increase the interaction of aliphatic carbons, but it does bring about an increase of 0.1 to 0.2 kcal in the specific interactions due to pi-electron systems. Acid washing also causes a decrease in the interactions due to aromatic substituents. This latter observation may be deceptive; the real effect may be that the enhanced pi-electron interaction amplifies substituent effects that are related to electron withdrawal.[21]

Several trends are observed for the functional group free energies in Table XI. First, both types of alumina separate <u>cis-trans</u> olefin isomers, while neither Porasil nor Florisil indicate any differentiation. With columns modified by 10% NaCl, the differential interactions for aliphatic carbons and pi-electron bonding systems follow the series Porasil $\leqslant$ F-1 $<$ Florisil. For alkyl-substituted benzenes the order of interactions is Porasil $<$ F-1 $\ll$ Florisil; the halogenated benzenes follow the order Porasil $\ll$ Florisil $<$ F-1. Separation of <u>cis-trans</u> isomers of olefins is effected in the order F-1 $\gg$ Florisil.

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When F-1 alumina is acid-washed prior to modification with Na_2SO_4 the interactions by pi-electron systems are enhanced and the resolution of <u>cis</u>-<u>trans</u> olefins is improved.[12] Interactions by halobenzenes are reduced, but acid-washing has no effect on aliphatic carbon and alkyl benzene interactions.

Because both the salt coating and the underlying surfaces are involved in the adsorption of a compound, a series of coated and uncoated Porasil C columns have been used to separate and study the two effects.[19] Tables XII and XIII summarize the variations of the thermodynamic parameters for porous silica caused by adding a salt coating and by silizaning the surface. Coating Porasil C with 10% Na_2SO_4 increases the aliphatic carbon (C_H), π, and φ-X free energy contributions. In contrast, silizaning decreases the C_H, π, and aromatic alkyl substituent (φ-Alk) free energy contributions while increasing the φ-X contributions. These changes in free energy contributions are due to increases in C_H, φ-Alk, and φ-X enthalpy contributions and to large increases in the φ-Alk entropy contributions. The change in entropy contribution per halogen is increased by silizaning.

Combination of silizaning and a Na_2SO_4 coating has a negligible effect on the φ-Alk enthalpy contributions but increases the enthalpy contributions for C_H, π, and φ-X. The entropy contributions for φ-Alk, φ-X, and aliphatic π electron systems also are increased. The reduction of the free energy contributions for π electrons with silizaning supports the theory that π systems interact with surface hydroxyl groups because silizaning eliminates the hydroxyl bond. The effects of silizaning and salt-coating are reduced as the

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TABLE XII

Effects of Salt Modification and Silizaning of Porasil C on Thermodynamic Parameters for Various Functional Groups
(Enthalpies in Kilocalories; Entropies in Entropy Units)

	10% Na_2SO_4				Uncoated			
			Silizaned				Silizaned	
x	$\Delta(-\Delta \underline{H})_x$	$\Delta(-\Delta \underline{S})_x$	$\Delta(-\Delta \underline{H})_x$	$\Delta(-\Delta \underline{S})_x$	$\Delta(-\Delta \underline{H})_x$	$\Delta(-\Delta \underline{S})_x$	$\Delta(-\Delta \underline{H})_x$	$\Delta(-\Delta \underline{S})_x$
o	1.33	16.69	0.61	15.95	0.05	13.28	-0.25	12.72
C	0.86	0.97	0.99	1.36	0.98	1.30	1.12	1.86
π_{term}	1.02	1.52	1.43	2.84	1.42	2.45	0.11	0.17
$\pi_{cis-trans}$	0.92	1.01	0.94	1.69	1.26	2.06	0.44	0.86
π_{conj}	1.26	1.72	1.38	2.44	1.61	2.62	1.06	2.12
π_{arom}	1.11	1.69	0.88	1.49	1.07	1.64	1.10	2.20
φ-CH_3	1.83	2.59	1.84	2.98	1.62	1.92	2.23	4.06
-Et	2.77	3.69	2.90	4.45	2.61	3.23	3.53	6.28
-iPr	3.44	4.46	3.49	5.23	3.15	3.84	3.81	6.42
-tBu	4.20	5.35	4.32	6.36	3.85	4.65	4.68	7.76
-CF_3	-0.81	-2.17	0.82	0.88	--	--	0.08	-0.45
-F	-0.90	-1.70	0.12	0.05	-0.80	-1.35	-1.50	-3.40
-Cl	-0.49	-1.74	1.08	1.15	0.01	-0.50	0.16	-0.72
-Br	0.22	-0.87	1.95	2.38	0.68	0.28	1.04	0.63
-I	1.01	0.08	3.08	3.97	1.56	1.38	2.07	2.20
-OCH_3	5.07	6.21	6.04	8.69	--	--	--	--
-NO_2	9.36	12.02	9.71	12.98	--	--	--	--
-CN	10.78	13.18	10.50	13.73	--	--	--	--
-CHO	8.82	9.61	10.38	13.69	--	--	--	--

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TABLE XIII

Effects of Salt Modification and Silizaning of Porasil C on Free Energies of Adsorption for Various Functional Groups $(\Delta(-\Delta \underline{G})_x$, at 500 $^\circ$K, in Kilocalories)

x	10% Na_2SO_4			Uncoated			σ_p[10]
		Silizaned	Δ		Silizaned	Δ	
o	-7.01	-7.36	0.35	-6.59	-6.61	0.02	
C	0.38	0.31	0.07	0.33	0.19	0.14	
π_{term}	0.26	0.01	0.25	0.19	0.03	0.16	
$\pi_{cis-trans}$	0.41	0.10	0.31	0.23	0.00	0.23	
π_{conj}	0.40	0.16	0.24	0.29	0.00	0.29	
π_{arom}	0.26	0.13	0.13	0.24	0.00	0.24	
φ-CH_3	0.53	0.35	0.18	0.65	0.19	0.46	-0.17
-Et	0.92	0.67	0.25	0.99	0.39	0.60	-0.15
-iPr	1.21	0.88	0.33	1.23	0.60	0.63	-0.15
-tBu	1.53	1.13	0.40	1.53	0.80	0.73	-0.20
-CF_3	0.29	0.38	-0.09	--	0.31	--	+0.54
-F	-0.04	0.10	-0.14	-0.12	0.19	-0.31	+0.06
-Cl	0.39	0.51	-0.12	0.27	0.53	-0.26	+0.23
-Br	0.66	0.76	-0.10	0.53	0.72	-0.19	+0.23
-I	1.01	1.09	-0.08	0.87	0.97	-0.10	+0.18
-OCH_3	1.96	1.70	0.26	--	--	--	-0.27
-NO_2	3.35	3.22	0.13	--	--	--	+0.78
-CN	4.19	3.64	0.55	--	--	--	+0.66
-CHO	4.01	3.53	0.48	--	--	--	+0.50

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temperature is lowered to 60 °C. While inorganic salt-coated Porasil surfaces are generally stable, silizaned surfaces decompose with time to such an extent as to make them impractical for most applications of gas-solid chromatography. In general, reduction of column temperature enhances the free energy contributions of π systems relative to those for C_H.

The ultimate use of the thermodynamic approach is to be able to predict sample separations. As an example, a set of predictions has been made for an acid-washed Na_2MoO_4 F-20 alumina column at 200 °C. The experimental separation of this group of compounds is illustrated by Figure 5 and provides the data for the comparison of predicted and experimental retention volume ratios that are summarized in Table XIV.[16]

The effectiveness of salt-modified Porasil columns for the separation of isomeric hydrocarbon mixtures is illustrated by Figure 6.[19] The chromatogram for this

TABLE XIV

Comparison of Predicted and Experimental Retention Volumes at 200 °C for an Acid-Washed 10% Na_2MoO_4 F-20 Alumina Column

	$\underline{V}_{\underline{R}}(x)/\underline{V}_{\underline{R}}(\text{pentane})$	
x	Predicted	Experimental
hexane	2.21	2.23
trans-2-pentene	1.52	1.57
cis-2-pentene	1.84	1.92
1-pentene	1.74	1.80
1-hexene	3.84	4.00
benzene	9.95	10.50
chlorobenzene	25.68	26.63
toluene	27.35	27.31

22-component mixture dramatically illustrates the lack of correlation between boiling point and retention volume. The quality of the separation is particularly impressive for a column that is only 3 feet long and for an analysis time of less than 2 minutes.

Certain columns have particularly large contributions for aromatic methyl and halogen substituents. Such columns probably have the greatest potential for separating the isomers of xylene and disubstituted halobenzenes. Although attempts to resolve the xylene

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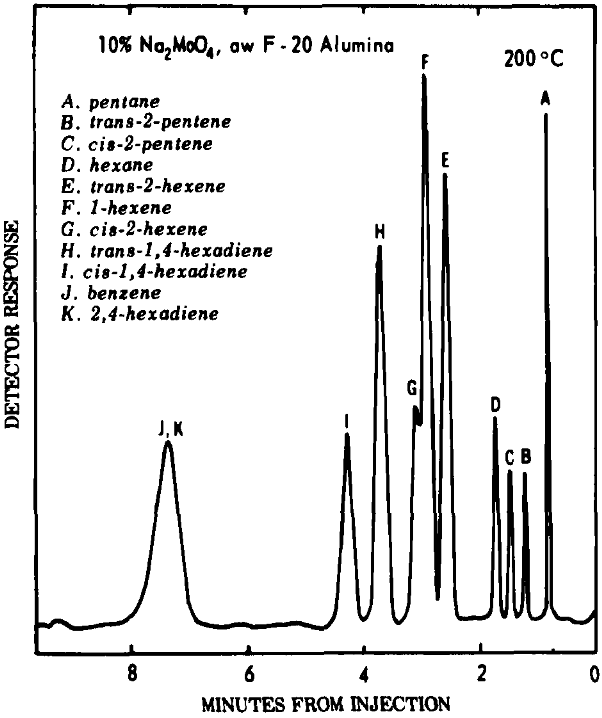

FIGURE 5

Gas chromatogram for an eleven-component isomeric mixture of five- and six-carbon unsaturated hydrocarbons with a 3-ft x 1/8 in. column.

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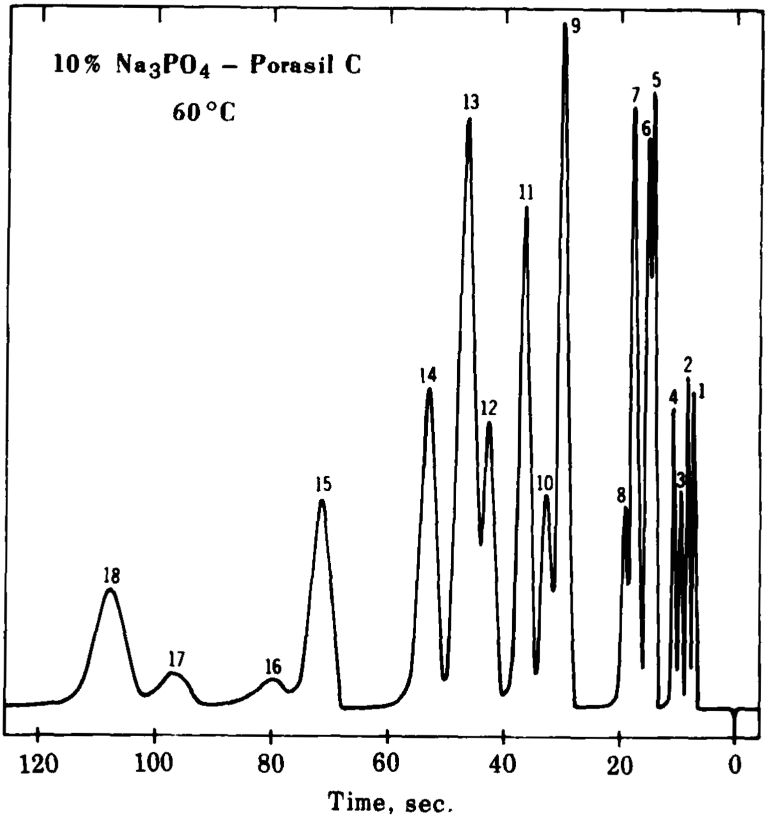

FIGURE 6

Gas chromatogram for a 22-component hydrocarbon mixture with a 3-ft x 1/8 in. column.

Boiling points indicated in parentheses: Peak No. 1. methane (-161); 2. ethane (-89); 3. ethylene (-104); 4. propane (-45); 5. acetylene (-84); 6. cyclopropane (-33); 7. propene (-48) and butane (-1); 8. propadiene (allene) (-35); 9. isobutane (28); 10. pentane (36) and cyclopentane (49); 11. 1-butene (-6); 12. trans-2-butene (1); 13. isobutylene (-7) and cis-2-butene (4); 14. 1,3-butadiene (-4); 15. methylacetylene (-23); 16. 1-pentene (29); 17. trans-2-pentene (36); 18. cis-2-pentene (38) and 2-methyl-1-butene (39).

isomers have been unsuccessful, the separation of the dichlorobenzene isomers is accomplished with an acid-washed, Na_2MoO_4-modified F-20 alumina column (Figure 7).[16]

The order of elution of the dichlorobenzenes can be rationalized by noting that the inductive effect of the electronegative halogens decreases the pi-electron density of the aromatic nucleus and thereby decreases the pi-electron interaction. Thus, the dichlorobenzene isomers with the greater ability to withdraw electrons from the aromatic ring should be retained less strongly. Because the inductive effect decreases with distance from the substituent, the meta and para isomers (with more ortho centers available) should be retained less

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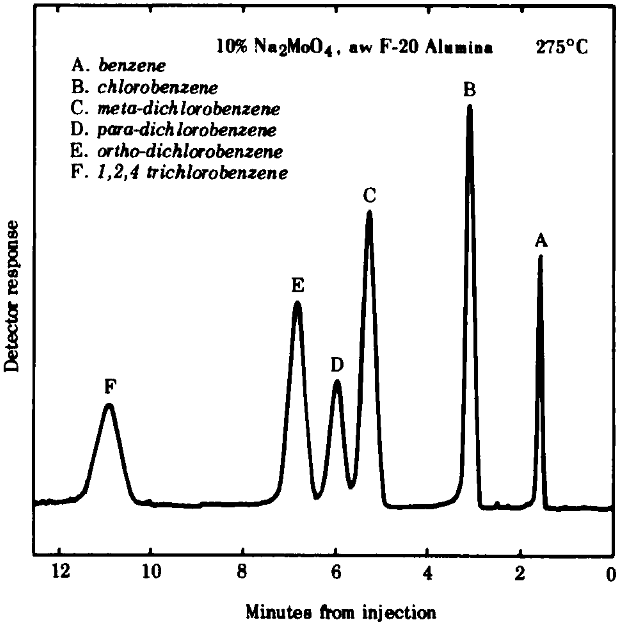

FIGURE 7

Gas chromatogram for benzene and chlorobenzenes with a 3-ft x 1/8 in. column.

than the ortho isomer. Either a steric factor or resonance effects probably accounts for the reduced interaction of the meta isomer relative to para dichlorobenzene

Mechanisms of Interactions. Until recently a quantitative relationship between molecular structure and the interactions which have been termed specific and nonspecific had not been identified. Kiselev[22,23] had shown the importance of dispersion interactions in certain cases and had proposed a qualitative scheme for classifying adsorbate molecules and adsorbents. However, King and Benson were the first to advance a quantitative theory for nonspecific interactions.[24,25] This has been tested by salt-modified gas-solid chromatography[26] and confirmed to be a useful molecular basis for such interactions.

The King and Benson theory for electrostatic interactions at gas-solid surfaces[24,25] proposes that the energy of interaction, φ_{att}, is given by

$$\varphi_{att} = \frac{\alpha}{2} \frac{C_{eff}}{Z^4} \qquad (9)$$

or

$$\varphi_{att} = \frac{\alpha}{2} E_z^{\,2} \qquad (10)$$

where α is the polarizability of the adsorbed molecule, C_{eff} the surface charge, Z the distance of the molecule from the surface, and E_z the electric field normal to the surface. The theory predicts that the inert gases and methane will interact with the adsorbent in direct relation to their polarizability. This has been confirmed experimentally for alumina at room temperature and above.[25] The applicability of the theory to other gas-solid interactions has been suggested.[25]

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A test of the King and Benson theory as it relates to salt-modified aluminas and silicas has been undertaken to define more fully the controlling factors in gas-solid chromatography.[26] A plot of log $\underline{V}_{\underline{s}}^{\underline{T}}$ *vs.* polarizability for the inert gases, oxygen, and methane on a 10% sodium-chloride coated column of acid-washed H-151 alumina yields a straight line. Plots for other salt-modified alumina columns have the same general appearance. The data indicate a direct correlation at three different temperatures, which is in accord with the theory of King and Benson.[25] Nitrogen is above the lines because of its specific interaction due to the triple bond; the deviation increases as the temperature is reduced to give an increased interaction.

The characteristics of the salt-coated Porasil columns are illustrated by a plot of log $\underline{V}_{\underline{s}}^{\underline{T}}$ *vs.* polarizability for a 10% NaCl-coated column, which gives a straight line for argon (oxygen and nitrogen), krypton, and xenon; methane is off the line. This also is true for preliminary studies on a graphitized carbon (Graphon) column. Thus, methane exhibits less interaction than it should according to the theory of King and Benson.[24]

These results indicate that the inert gases are adsorbed in a fashion that is consistent with the King-Benson theory.[24] However, the adsorption of methane on Porasil appears to be an exception to their theory. To fit methane onto the straight line for Ar, Kr, and Xe would require that it have a polarizability of 24.0×10^{-25} cm, which is significantly below the measured value of 26.0×10^{-25} cm. One way to explain this anomaly is to characterize the surface interaction by an "effective polarizability." The latter represents the polarizability of a molecule in relation to the surface to which the molecule is adsorbed. Thus, gas-solid chromatographic data provide a means of evaluating such a quantity. The diminished interaction of methane implies that the acidic surface of Porasil[27] exerts a repulsive force to the hydrogen atoms of methane to give an "effective polarizability" which is less than its measured polarizability. The basic surface of aluminas[28] does not exert such a repulsive force, and therefore the "effective polarizability" of methane on salt-modified aluminas is equal to its polarizability. The inert gases have no acidic or basic character and therefore their "effective polarizability" always is equal to their polarizability. Graphon has a slightly acidic surface[29] and preliminary experiments indicate that methane's "effective polarizability" on Graphon is 24.6×10^{-25} cm. Therefore, methane is repulsed less by the Graphon surface than the more acidic Porasil surface. The concept of "effective polarizability" allows one to describe the interaction of methane with the acidic surface of Porasil and Graphon and still be consistent with the basic ideas of the King and Benson theory. Thus, the nonspecific interaction of sorbate molecules with salt-modified aluminas and Porasils can be described quantitatively as the free energy of adsorption due to the "effective polarizability" of a molecule on the surface.

Another study[21] has illustrated the relationship between the logarithm of the capacity factor and the molar refraction for normal alkanes. Molar refraction is related to polarizability by a constant and is a quantity that is more readily available from the literature for organic compounds. Figure 8 gives the varia-

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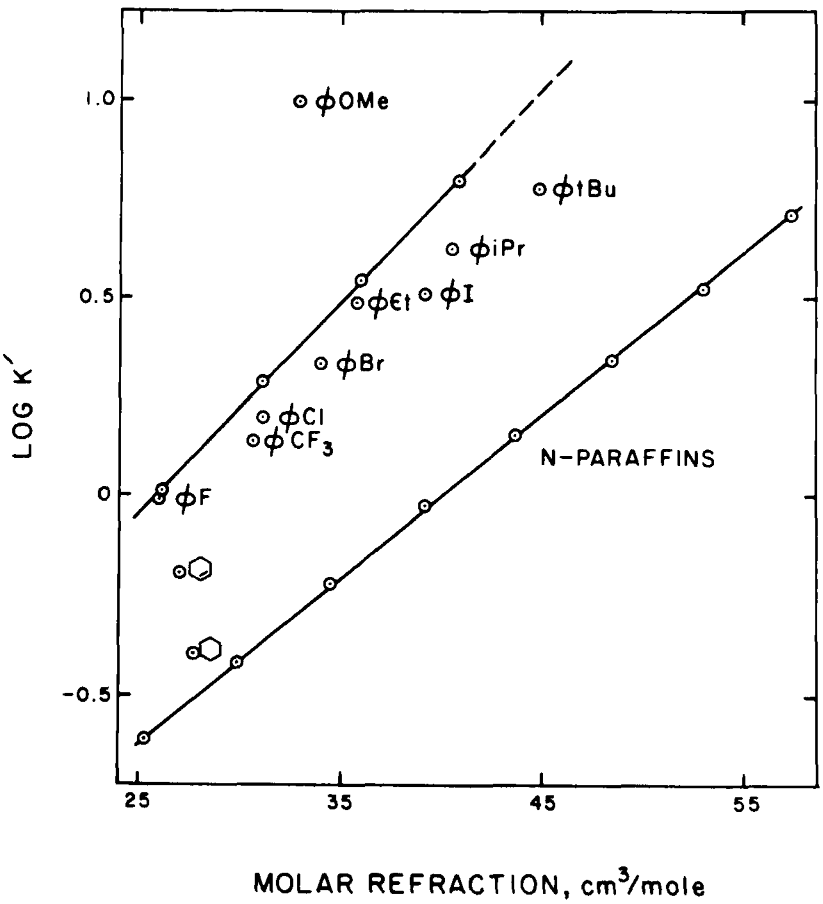

FIGURE 8

Logarithms of capacity factors, k', for a series of hydrocarbons vs. their molar refractions using a 10% wt/wt Na_2SO_4-modified Porasil C(100-120 mesh) column at 200 °C.

tion of the logarithm of the capacity factor, k', with the room-temperature molar refraction, R, for several groups of organic compounds. The straight lines that are obtained for methyl-substituted benzenes and normal

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paraffins imply that for these essentially nonpolar compound groups the free energy of the adsorption is a linear function of the polarizability. Again, the separation between the two lines appears to be due to differences in degrees of specific interaction.

The deviation of many of the substituted benzenes from the line defined by the methyl benzenes indicate the electron withdrawing or donating effects of the substituent groups also are important. The dipole moment may play a part, but if the pi-electron density holds the compound approximately parallel to the surface then the angle for dipole-dipole interactions is not favorable.

A relationship between aromatic electron density and adsorptive interaction is apparent from the data for silizaned Porasil (Table XII). On this column the $\pi_{\underline{\text{aromatic}}}$ free energy contribution is zero at 500 ^{o}K and the φ-Alk free energy contribution per substituent carbon is equal to the C_H contribution. Therefore, only the ring carbons and substituent atoms contribute to the free energy of adsorption; the aromatic system does not contribute. Because the free energy of adsorption on unmodified Porasil C includes contributions from the aromatic system, the difference in free energies between unmodified and silizaned Porasil C should provide a measure of aromatic electron density. This is illustrated by Figure 9, which is a Hammett plot relating aromatic electron density with differences of free energies. The quantity $\sigma_{\underline{p}}$ is proportional to aromatic π-electron density because of a para substituent, while $\sigma_{\underline{I}}$ is proportional to the inductive component of aromatic electron density for such a substituent.[30] The

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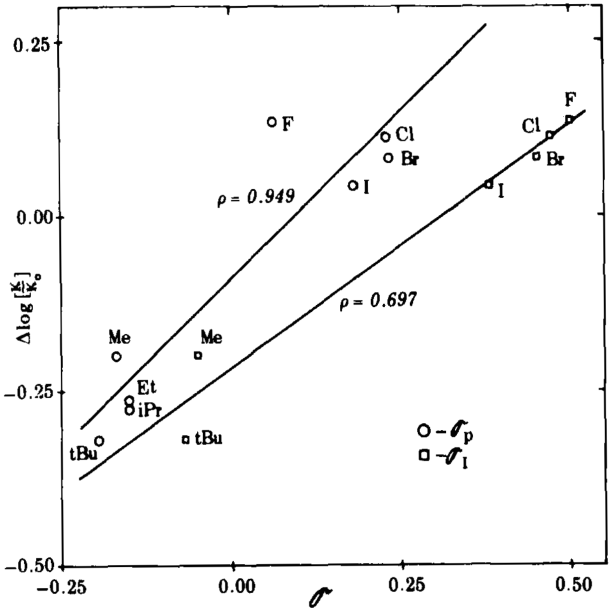

FIGURE 9

Hammett plot of $\Delta \log \left[\frac{K}{K_o}\right]$ vs. σ_p and σ_I

K, substituent distribution constant on Porasil C; K_o, substituent distribution constant on silizaned Porasil C; σ_p, para substituent constant; σ_I, inductive contribution to substituent constant.

free energy differences are related to the relative distribution constants by the expression

$$\Delta \log \left[\frac{K}{K_o}\right] = \log\left[\frac{K}{K_o}\right]_{\varphi R} - \log\left[\frac{K}{K_o}\right]_{\varphi H} = \frac{\Delta[\Delta(-\Delta G)]}{2.3RT} \qquad (11)$$

where K is the distribution constant on Porasil C, K_o the distribution constant on silizaned Porasil C, and $\Delta[\Delta(-\Delta G)]$ the free energy difference betwen unsilizaned and silizaned Porasil C.

The correlation is much better when σ_I values are used, which implies that inductive effects are more important than resonance effects for adsorptive interactions. The correlations are quite good, especially in view of the assumption that the interactions of the aromatic substituents are identical on both silizaned and unsilizaned surfaces. Furthermore, the σ values are for disubstituted molecules while the gas chromatographic data are for monosubstituted systems. Other specific interactions which have been tabulated are those olefinic bonds (see for example Table III). An interesting point is the large differences observed for such bonds in various environments. Nonconjugated, conjugated, and aromatic pi-electron systems have significantly different specific enthalpies and entropies. Isolation of these specific quantities makes it possible to ascertain how a given molecular pi-electron system interacts with an adsorbent and therefore provides data about the molecular configuration and its orientation with respect to the adsorptive surface.[15]

Extensive data are available concerning the structure of the saturated and unsaturated cyclic hydrocarbons from cyclopentane through cyclooctatetraene (COT). With the exception of benzene, studies of the adsorption for most of these compounds have been limited to graphitized carbon.[31] Because the adsorption of COT and its related compounds (as well as of the C_7, C_6, and C_5 cyclic hydrocarbons) had not been studied, a detailed chromatographic investigation of their retention in relation to known structures has been made.[15]

The structure of COT has been a subject of controversy because spectroscopic data support both crown and

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tub forms.[32-35] Later work tends to support the latter conformation[36] with the tub rapidly inverting and passing through a planar intermediate.[37,38] In the tub form, the double bonds, while formally conjugated, have almost no overlap because adjacent bonds are skewed. Hence, these bonds should exhibit adsorption interactions characteristic of isolated double bonds if the adsorbed conformation resembles that found in the vapor phase. Chromatographic measurements made on COT and related hydrocarbons should provide evidence for the more probable configuration in the adsorbed state. A comparison of enthalpy and entropy data for the adsorption of cycloalkanes and normal alkanes also should provide additional structural correlations.

The retention volumes, $\underline{V}_{\underline{R}}$, of several homologous series of cyclic hydrocarbons on a Porasil C column are illustrated in Figure 10. Because log $\underline{V}_{\underline{R}}$ is related linearly to the free energy of adsorption, the data indicate that both linear and cyclic alkanes, as well as the cyclic alkenes, increase linearly in free energy of adsorption with the number of methylene groups in the molecule. The vertical distance between any two points on the plot is linearly related to the difference in free energy between the two compounds.

An important observation is that the enthalpies and entropies of interaction for 1,3-cyclooctadiene are only slightly larger than those for cyclooctene, while those for the 1,5-isomer are two to three and one-half times as large as for the mono-olefin. To a lesser degree a similar preferential set of interactions is observed for the 1,4-isomer relative to the 1,3-isomer of cyclohexadiene. Furthermore, 1,3,5,7-cyclooctatetraene has enthalpies and entropies of interaction that are smaller than for the 1,5-isomer of cycloocta-

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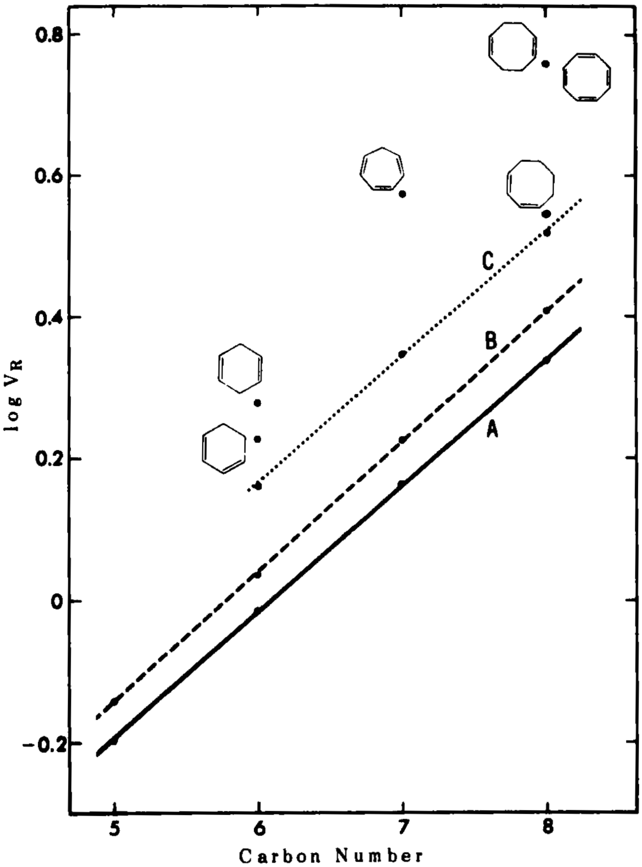

FIGURE 10

Logarithm of retention volumes vs. carbon number for normal alkanes (A), cyclic alkanes (B), cyclic monoalkenes (C), and related compounds as indicated on a 10% Na_2SO_4-Porasil C column at 225 °C.

diene on the Porasil C column, and approximately the same as the diene on the alumina column. The interactions of 1,3,5-cycloheptatriene are almost identical to those for the C_8-tetraene and quite similar to those for benzene.

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Thus, geometric and steric factors govern the extent to which the olefinic pi orbitals can interact with the adsorbent, especially in the case of the Na_2SO_4-Porasil C column. In the case of the C_8 olefins the 1,3-diene isomer has a geometry such that essentially only one pi bond can interact; in contrast, the 1,5-diene isomer's configuration is sufficiently idealized that its two pi bonds interact more than three times as extensively as the pi bond of cyclooctene and to the same degree as the tetraene. This latter consideration implies that only the 1,5-pi bonds of the tetraene are in an orientation that permits interaction with the adsorbent. Another interesting point is that the pi-orbital interaction of 1,3,5-cycloheptatriene is the same as that for cyclooctatetraene; this is reasonable in that the gas phase configuration for the 1,3,5-triene portion of the two molecules is identical.[36,39] The thermodynamic parameters for the cyclohexadienes indicate that the 1,4-isomer interacts about twice as extensively as cyclohexene, whereas the 1,3-isomer has a geometry that causes the interaction to be one and one-half times as great.

Consideration of the geometric effects on interaction indicates that the pi orbitals must be perpendicular to the adsorbent surface for maximum interaction. Thus, the pi bonds of 1,5-cyclooctadiene and 1,4-cyclohexadiene are parallel and in a configuration that allows them to lie on a plane. Likewise, the 1,5-pi bonds of cyclooctatetraene and of 1,3,5-cycloheptatriene are parallel to allow maximum interaction. Molecular models indicate that the 3- and 7-pi bonds in these two molecules are completely out of the plane for the 1,5-pi bonds and therefore cannot interact effectively with the surface.

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Molecular and Structural Parameters. The early studies by our group left unanswered questions concerning specific effects due to halogens and dipole moments. For example, in the case of aliphatic compounds on porous silica, anomalies occur for the specific carbon contribution when the carbon substituents are varied.[19] Attempts to predict the specific retention volumes of multi-substituted molecules also fail when the specific thermodynamic parameters for halogens are used. Consequently, a more rigorous evaluation of adsorption in terms of the molecular parameters of the sorbate became necessary.

The contribution of a molecule's molar refraction, dipole moment, and nonbonding electrons to specific interactions with the adsorbent has been the subject of a detailed investigation.[40] The adsorbents included Graphon, 10% Na_2SO_4 on acid-washed F-1 alumina, and 10% Na_2SO_4 on porous silica (Porasil C); hydrocarbons and halogenated methanes were used as the sorbate molecules. By relating adsorptive interactions to molecular parameters, the specific retention volumes of other compounds can be predicted. In cases where the molecular parameters change with changes in conformation, the conformation of the adsorbed molecule can be discerned. This approach to the thermodynamics of adsorption also provide a means of studying the nature of adsorbent surfaces.

The coefficients of the three molecular parameters (molar refraction, dipole moment, and specific halogen effects), in terms of adsorption thermodynamics, have been obtained by analyzing the retention volume data for a set of model compounds with a least squares program[41] translated into APL and run on an IBM 360/50 computer. These coefficients are summarized in Table XV A. The

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TABLE XV

Contributions of Molecular Parameters to Standard State Enthalpies and Entropies of Adsorption on 10% Na_2SO_4 on Porasil C

A. Parameter Dependence

Molecular Dependence	$-\Delta H^o$	$-\Delta S^o$
Zero point	0 Kcal	2.48 e.u.
Molar refraction (R)	0.276 Kcal/R	0.443 e.u./R
Dipole moment (μ)	2.131 Kcal/debeye	3.478 e.u./debeye
Chlorines capable of specific interactions	0.263 Kcal/Cl	0.085 e.u./Cl

B. Comparison of Calculated and Experimental Thermodynamic Quantities

				Calcd		Exptl	
Compound	R	μ	Cl	$-\Delta H^o$	$-\Delta S^o$	$-\Delta H^o$	$-\Delta S^o$
C_5	24.3	0	0	6.70	13.25	6.81	13.20
CH_2Cl_2	16.3	1.60	2	8.43	15.44	8.34	15.19
$CHCl_3$	21.2	1.01	3	8.79	15.65	8.75	15.75
CCl_4	25.9	0	3	7.94	14.22	8.02	14.48
CH_2Br_2	21.4	1.43	~3	9.74	17.20	9.76	17.00
CF_4	7.12	0	0	1.96	5.63	1.77	5.53
CF_2Cl_2	15.9	0.51	0	5.47	11.30	5.25	11.04
CHF_2Cl	11.08	1.42	0	6.06	12.30	6.26	12.80

compounds, their molar refractions (R), dipole moments (μ), the number of specific chlorine interactions, and the calculated $-\Delta H^{o}$ and $-\Delta S^{o}$ values in comparison to those obtained experimentally are summarized in Table XV B.

Experiments with the Porasil C column for multi-halogenated ethanes, propanes, and longer carbon chains yield satisfactory agreement between the experimental values and those predicted from the coefficients in Table XV in all cases except where the dipole moment is strongly dependent on molecular conformation. In those cases, the calculated retention volumes are low.

Calculations for alternative conformers indicate that the energy gained from the increased interaction of the unfavorable conformer is greater than the energy difference between the favorable and unfavorable conformers. An illustrative example is 1,2-dichloroethane. At 412 °K in the gaseous phase, its dipole moment is 1.46 D, which for the Porasil column gives calculated values for $-\Delta H^{o}$ of 9.43 kcals and for $-\Delta S^{o}$ of 17.05 cals-degree^{-1}. These quantities predict a retention volume at 400 °K of 10.0 ml. The experimental results are $-\Delta H^{o}$, 10.60 kcals, and $-\Delta S^{o}$, 17.98 cals-degree^{-1}, and a retention volume of 25.6 ml. However, by assuming that the molecule adsorbs on the surface as the gauche conformer (Figure 11) new values are obtained for the dipole interaction.

Because Cl(1) is approximately 40° from perpendicular with the surface, its dipole interaction is 1.43 D (1.87 D x cos 40°). Cl(2) is about 60° from perpendicular to the surface which gives an interaction of 0.94 D (1.87 D x cos 60°); when added to Cl(1), this gives a total dipole interaction of 2.37 D. If the original gas

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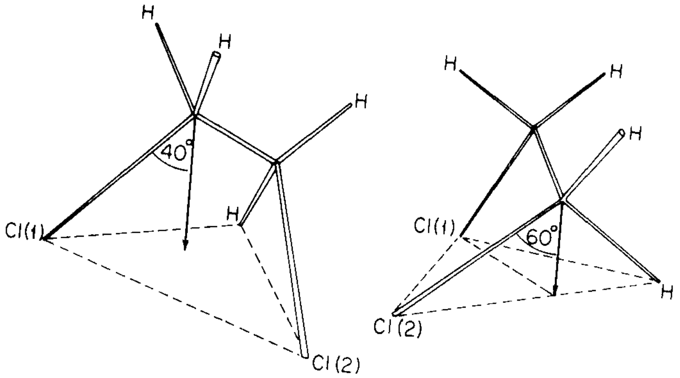

FIGURE 11

Proposed conformation for 1,2-dichloroethane when adsorbed on a Porasil C surface.

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phase dipole of 1.46 D is replaced with this number and the gauche Cl-Cl repulsive interaction of 1.1 kcals[42] is subtracted, the result gives a $-\Delta \underline{H}^{o}$ value of 10.27 kcals. Similarly, a new calculated entropy is obtained. However, because there are four equivalent ways the gauche conformer can sit on the surface, a factor of $\underline{R}$ ln 4 (equal to 2.75) must be subtracted to give a $-\Delta \underline{S}^{o}$ value of 17.47 cals-degree^{-1}. These new values predict a retention volume of 22.8 ml at 400 ^{o}K, which is in good agreement with the experimental value.

Examples of other molecules which appear to undergo conformational change upon adsorption are 1,2-dichloropropane, 1,1,2-trichloroethane, 1,2,3-trichloropropane, and 1,3-dichloropropane. This conclusion is based on models of adsorptive conformers which yield calculated enthalpies and entropies of adsorption in agreement with the experimental values.

The most practical aspect of the results is the ability to predict retention volumes on the basis of molecular structure after running a small series of model compounds. Table XVI gives the predicted logarithms of the corrected retention volumes of a series of fumigants compared to those found experimentally. Figure 12 illustrates the resulting chromatogram. A significant factor in the accuracy of the predicted retention volumes is the uncertainty of the values for the molecular parameters. Where the use of "effective" dipole moments is noted, the compounds

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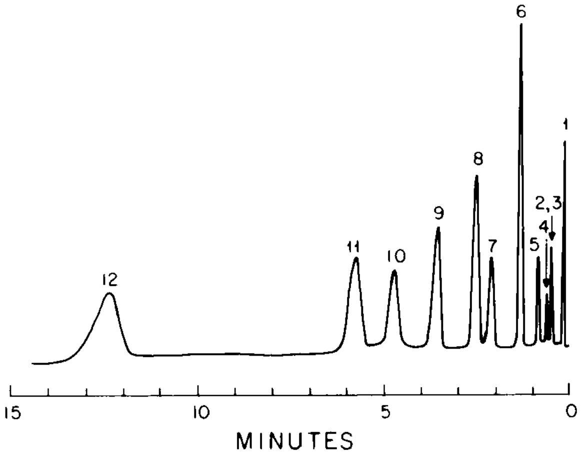

FIGURE 12

Gas chromatogram for a series of fumigants on a 10% wt/wt Na_2SO_4-Porasil C column at 125 °C. Sample components: 1, CH_3Cl; 2, CH_2Cl_2; 3, CCl_4; 4, $CHCl_3$; 5, CCl_3CH_3; 6, $BrCH_2CH_2CH_3$; 7, $ClCH_2CH_2Cl$; 8, $BrCH_2(CH_2)_2CH_3$; 9, $ClCH_2CHClCH_3$; 10, $BrCH_2(CH_2)_3CH_3$; 11, $Cl_2CHCHCl_2$; 12, $BrCH_2CH_2CH_2Br$.

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TABLE XVI

Predicted Thermodynamic and Log $\underline{V_R}$ Values for a Series of Fumigants Compared to Experimental Log $\underline{V_R}$ Values on 10% Na_2SO_4 on Porasil C at 125 °C

				Calculated			Experimental
Compound	$\underline{R}$	μ	Cl	$-\Delta\underline{H}^o$	$-\Delta\underline{S}^o$	Log $\underline{V_R}$[a]	Log $\underline{V_R}$
CH_3Cl	11.2	1.87	1	7.33	14.05	0.51	0.33
CH_2Cl_2	16.3	1.60	2	8.43	15.44	0.81	0.77
CCl_4	25.9	0	3	7.94	14.22	0.81	0.77
$CHCl_3$	21.2	1.01	3	8.79	15.65	0.97	0.88
CCl_3CH_3	26.1	1.78	3	11.78	20.49	1.55	1.02
$BrCH_2CH_2CH_3$	23.7	1.78[b]	1.5	10.73	19.31	1.23	1.21
CH_2ClCH_2Cl	21.0	2.37[b]	2	10.27	17.47	1.38	1.40
$BrCH_2(CH_2)_2CH_3$	28.3	1.70[b]	1.5	11.83	21.07	1.45	1.49
$ClCH_2CHClCH_3$	25.6	2.37[b]	2	11.54	19.48	1.64	1.62
$BrCH_2(CH_2)_3CH_3$	33.1	1.80[b]	1.5	13.36	23.54	1.75	1.76
$CHCl_2CHCl_2$	30.6	1.60[b]	3	12.64	20.49	2.02	1.85
$BrCH_2CH_2CH_2Br$	31.4	2.80[b]	3	15.43	26.38	2.27	2.18

[a] Log $\underline{V_R} = (-\Delta\underline{G}^o - 11.33\ \underline{T} + 2.3\ \underline{RT} \log A)/2.3\ \underline{RT}$.

[b] Effective dipole moment.

either contain bromine (which models indicate is forced about 35° from perpendicular to the surface because of its large size) or the molecule requires a conformational change in its adsorbed state (as previously exemplified by 1,2-dichloroethane).

The converse also should be possible. With the accumulation of enough data to pick the best columns, the structure of a compound could be determined by its retention on a series of columns. This should be feasible in gas-solid chromatography because of the long term column stability relative to gas-liquid columns as well as the greater ease of reproducibility when duplicate columns are prepared.

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Surface Complexes. Another possible type of specific interaction with salt-modified surfaces is the formation of complexes with the coating salt.[18] Because previous work[43] has established that the stability constants of weak charge-transfer and hydrogen-bonded complexes can be evaluated from gas-liquid chromatographic measurements, a similar approach has been used for the study of gas-solid complexes on salt-coated silica gel and Graphon. A group of substituted aromatic molecules have been studied at three different temperatures in terms of their interaction with a $LaCl_3$ coating.

Because salts like $LaCl_3$ contain partly filled d or f shells and are strong Lewis acids, they should form complexes of varying strength with electron donor molecules. This adds another column parameter that may be varied to achieve more selective analytical separations.

Consideration of the data in Figure 13 indicates that the interactions of aromatic molecules are significantly greater when $LaCl_3$ is present on the silica

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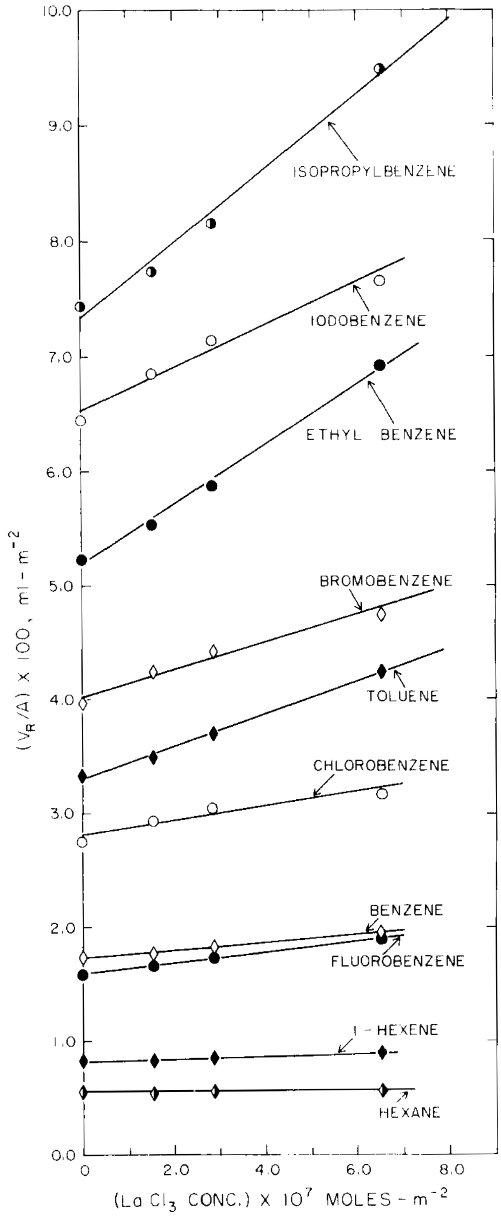

FIGURE 13

Specific retention volumes for a series of compounds as a function of the surface concentration of $LaCl_3$ on silica gel at 200 °C. NaCl used as the diluent; all columns coated with 10% by weight of salt (NaCl and/or $LaCl_3$).

gel surface. The linear slopes of the curves of Figure 13 also imply that the specific interactions are directly proportional to the surface concentration of $LaCl_3$, a condition indicative of complex formation.

Studies of complex formation in gas-liquid systems[43] have shown that the stability constants of the resulting complexes can be evaluated by the expression

$$K_R = K_R{}^o(1 + K_1C) \qquad (12)$$

where $\underline{K_R}$ and $\underline{K_R}^o$ are the partition coefficients of a solvate with a complexing solution and an inert solvent, respectively, $\underline{K_1}$ is the stability constant of the complex, and $\underline{C}$ is the concentration of ligand in the solution. This same expression is appropriate for the present gas-solid studies, but with $\underline{K_R}$ and $\underline{K_R}^o$ representing the partition coefficients of an adsorbate on a mixed $LaCl_3$-NaCl column and a NaCl column, respectively. For this system $\underline{K_1}$ represents the stability constant of the adsorbate-$LaCl_3$ complex and $\underline{C}$ is the surface concentration of $LaCl_3$ in the mixed coating (mole m^{-2}).

When the data of Figure 13 are analyzed by Equation 12, the stability constants of the $LaCl_3$-surface complexes can be evaluated; these are summarized in Table XVII. By determining the stability constants at three different temperatures, the enthalpies of complex formation, $-\underline{\Delta H_f}$, can be evaluated from the slopes for plots of log $\underline{K_1}$ vs. $1/\underline{T}$ (van't Hoff plots). The results of such analyses also are summarized in Table XVII.

Consideration of the data in Table XVII indicates that electron-donating substituents (alkyl groups)[19] enhance the interaction of the aromatic ring. The magnitude of the heats of complex formation, $-\underline{\Delta H_f}$, also

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TABLE XVII

Stability Constants and Heats of Formation of Aromatic-$LaCl_3$ Complexes

	Stability constant $\underline{K}_1$, at 200 °C (m^2-$mole^{-1}$)	Enthalpy of complex formation, $-\Delta\underline{H}_f$, at 200 °C (Kcal-$mole^{-1}$)
Benzene	2.09×10^5	3.6
Toluene	4.37×10^5	4.8
Ethylbenzene	5.06×10^5	4.8
Isopropyl benzene	4.43×10^5	4.5
Fluorobenzene	3.00×10^5	4.6
Chlorobenzene	2.17×10^5	2.8
Bromobenzene	2.84×10^5	3.1
Iodobenzene	2.75×10^5	6.6
1-Hexene	1.62×10^5	...

are consistent with the formation of metal-aromatic complexes. In contrast, there appears to be no specific interaction between hexane and $LaCl_3$ and only a slightly enhanced interaction with 1-hexene. Thus, the heat of adsorption for benzene on $LaCl_3$-coated silica gel is increased 5 kcal over its value on NaCl-coated silica gel while the heat of adsorption for hexane is less on $LaCl_3$ than on NaCl.

Thermal Activation of Silica. The nature of specific interactions also yields information about the surface of an adsorbent and how that surface changes with thermal and chemical pretreatment. Because the groups present at the surface of an adsorbent are highly dependent on its thermal and chemical pretreatment, investigations of the adsorption thermodynamics of salt-modified silica gel and porous silica beads provide

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insight to the nature of the active sites at the adsorbent surface and the adsorption processes. The thermodynamic studies also provide a basis for optimizing column activation temperatures for difficult analytical separations.

A series of substituted hydrocarbons have been chromatographed on each column at three different temperatures.[17] The resulting retention volume data, $\underline{V}_{\underline{R}}$, have been used to prepare plots of log $\underline{V}_{\underline{R}}$ vs. 1/$\underline{T}$, which permit evaluation of the contributions made by the various adsorbate functional groups to the enthalpy, entropy, and free energy of adsorption. Such calculations have been made for each adsorbent activation temperature. Figure 14 indicates the variation of the various functional group contributions to the differential free energy of adsorption, $\Delta(-\Delta \underline{G})$, with changing activation temperature of the silica gel. The smoothness of the curves is impressive; furthermore, the 450 and 550 °C data (Figure 14) are for measurements that were made after all the other evaluations. Schultze and Schmidt-Kuster[44] obtained a curve similar to the terminal π-bond curve of Figure 14 when they plotted the difference between the logarithms of the retention volumes of ethylene and ethane vs. the adsorbent activation temperature for a high surface area silica. The minima for the two curves occur at similar activation temperatures and are of similar depth.

From an analytical standpoint, the adsorbent activation temperature is an important parameter in column preparation and can be used to improve the separation of a difficult mixture. This is illustrated by the chromatograms in Figure 15. Separation of the mixtures is not possible at adsorbent activation temperatures of 400 or

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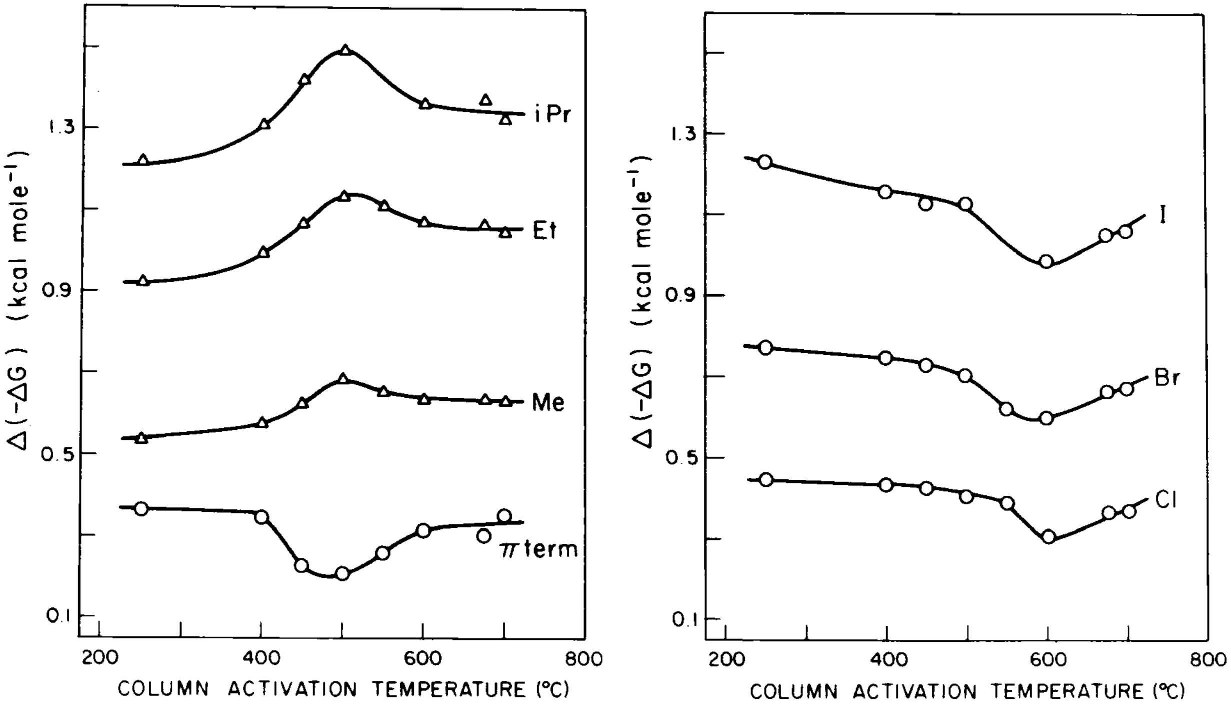

FIGURE 14

Dependence, for various functional groups, of free energy of adsorption, $\Delta(-\Delta \underline{G})$, at 500 °K on column activation temperature. Column, 10% NaCl-silica gel.

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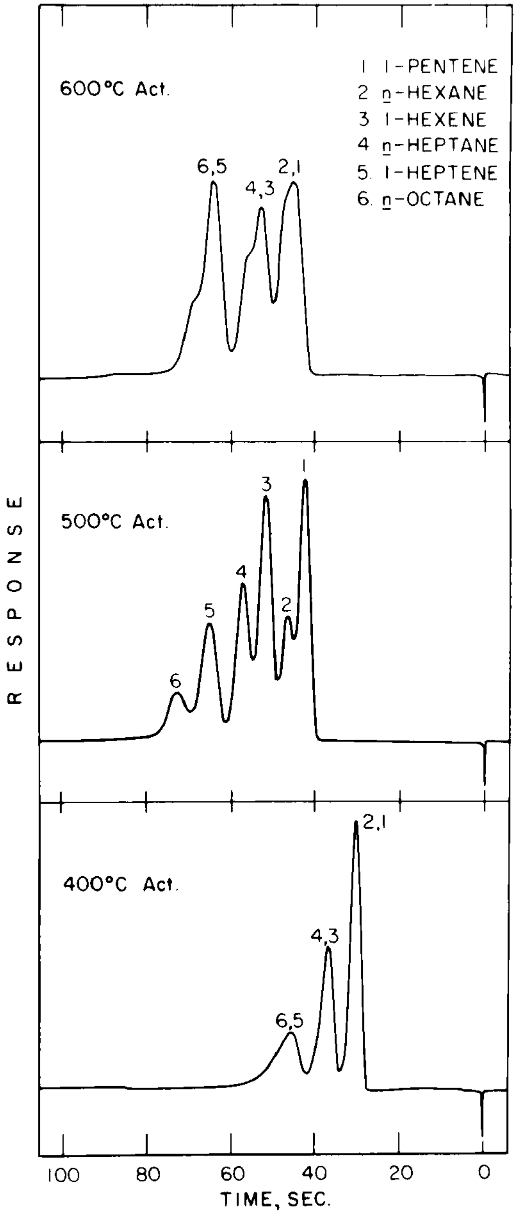

FIGURE 15

Gas chromatograms for six-component mixture with 10% NaCl-silica gel column activated at three different temperatures. Column temperature, 225 °C.

600 °C, but at an intermediate activation temperature of 500 °C reasonable resolution is achieved.

The data of Figure 14 also permit some conclusions to be made about the nature of the surface of the adsorbent and how it changes with thermal activation. Thus, adsorption of molecular water induces an enhanced dipole in the water molecule and weakened O-H bonds, which act as surface proton centers; the size of the dipole set up in the O-H bond depends on how tightly the unshared electron pair is held by the inner d orbital of the silicon. The latter is affected by the nature and number of the functional groups attached to the silicon. Thus, dehydration and chemical modification of the surface should change the coordination unsaturation of the surface atoms and, consequently, their acid strength.

Consideration of these arguments, infrared data, and adsorption data leads to the conclusion that the surface of the silica gel is covered initially by considerable amounts of molecular water bonded to surface silicon atoms (B) and surface hydroxyl groups; some free hydroxyl groups (A) also are present. Such a silica gel surface is illustrated by Figure 16. On raising the temperature of activation to 200 °C most of the hydrogen-bonded water appears to be removed with hydrogen bonds (C) forming between favorably placed single hydroxyls, as shown in Figure 17. Further heating to 500 °C probably removes all hydrogen-bonded water and most of the coordinated water molecules, and increases hydrogen bonding between hydroxyls. At 600 °C the hydrogen-bonded hydroxyls appear to condense to form surface siloxane linkages with a few single hydroxyls still present. Heating above 700 °C may remove the remainder of the free hydroxyls, but primarily causes a decrease in the surface area.

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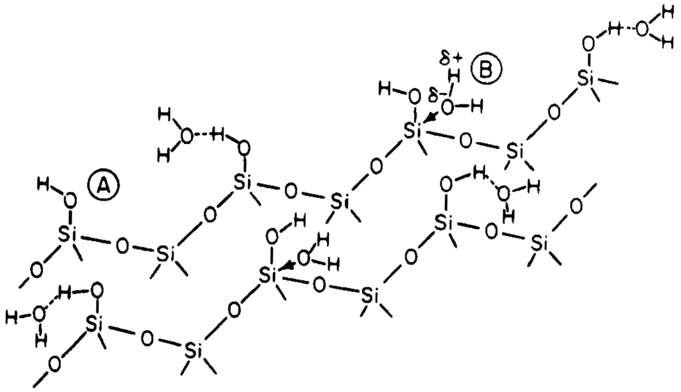

FIGURE 16

Surface of silica gel prior to activation.

On narrow pore silicas, most of the hydroxyls are present as reactive hydroxyls (C, Figure 17) and thus occur in groups of two or more, which can interact with each of the carbon atoms or double bonds of an unsaturated hydrocarbon. Such groups also cause strong adsorption of alkyl benzenes and, to a lesser extent, halo-

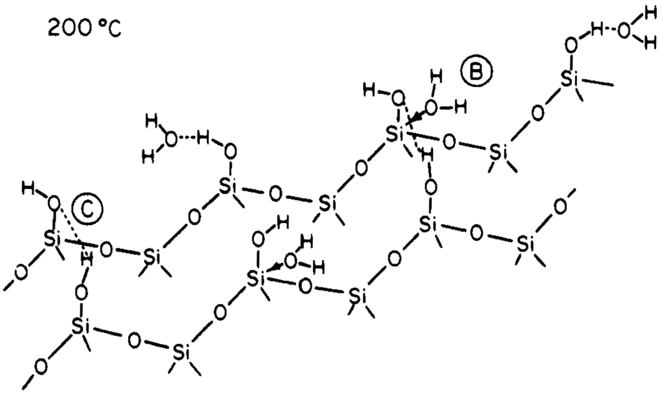

FIGURE 17

Surface of silica gel after activation at 200 °C.

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benzenes (due to the electron withdrawing effect of the halogen atom). Halobenzenes on the other hand should be strongly adsorbed at the proton centers (B, Figure 17) produced by the coordinated water molecules, because of the higher electron density at the halogen atoms. Little, if any, adsorption will take place at the single hydroxyls (A, Figure 16) while other more active proton centers are available.

As the activation temperature of the silica gel is raised from 200 to 500 °C, type (B) sites disappear and type (C) sites are formed. Thus, halobenzenes exhibit slightly reduced interactions at 500 °C, whereas alkyl benzenes are adsorbed more strongly. Further increase in the activation temperature causes type (C) sites to disappear and the interaction of both alkyl and halobenzenes with the surface to be reduced drastically.

All the adsorbents used in this work have been coated with NaCl, which appears to act as a conducting layer over the surface of the adsorbent and thereby attenuate the perturbations and forces due to the various adsorption sites.

Water Modification of Adsorbents. A final topic of recent interest can be described as water-modified gas-solid chromatography. Such a system is especially interesting in terms of mixed adsorption and absorption mechanisms.

The existence of adsorption on a liquid surface as well as absorption by the liquid was first shown by Martin[45] in a series of gas chromatographic experiments. The behavior of even more complex sets of retention mechanisms has been discussed since then by Purnell[46] and Urone.[47] When adsorption on the liquid surface and absorption by the liquid are the predominant interactions, the retention volume is governed by the relation

$$V_{gs}^{T} = K_A \times A_L + K_L \times V_L \qquad (13)$$

where $\underline{K_A}$ is the equilibrium constant for adsorption on the liquid surface (with units of ml/m^2), $\underline{A_L}$ the surface area of the liquid (m^2/g dry support), $\underline{K_L}$ the equilibrium constant for absorption by the liquid layer (ml/ml of liquid), and $\underline{V_L}$ the volume of the liquid phase (ml of liquid/g dry support).

Typical curves of retention volume vs. water content for organic compounds on wetted Porasil C are illustrated in Figure 18. All compounds show an increase in retention with decreasing water content.

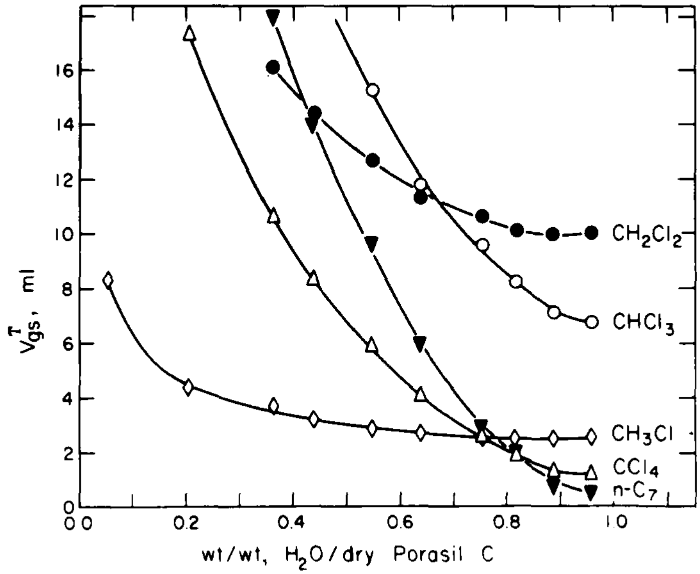

FIGURE 18

Specific retention volumes of organic compounds as a function of the water content of Porasil C.

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Also, the order of retention of the compounds changes drastically with water content. Figure 19 illustrates retention curves *vs.* water content for organic compounds on Chromosorb W. These are the same compounds that are illustrated in Figure 18. In contrast with the Porasil data all of the compounds except the alkanes exhibit a decrease in retention with decreasing water content. The retention order of the halomethanes does not change until the water content is less than 0.1 wt/wt water/ dry support.

Using experimentally determined values for V_{gs}^{T}, A_L, and V_L, a least squares fit has been used to determine K_A and K_L for compounds sorbed by water adsorbed on Porasil C in the region of 0.363 to 0.755

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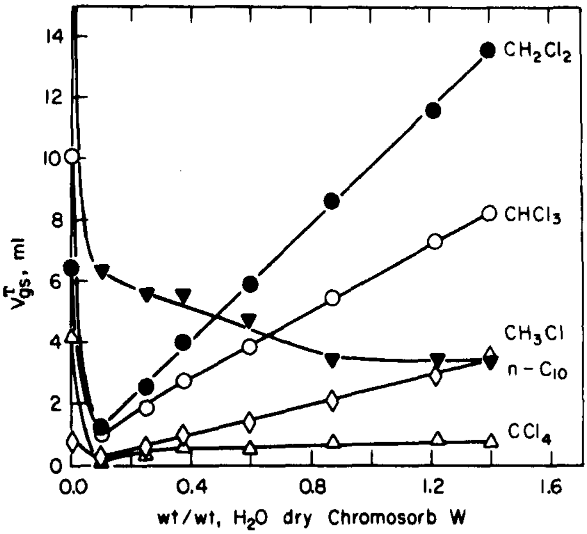

FIGURE 19

Specific retention volumes of organic compounds as a function of the water content of Chromosorb W.

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wt/wt water/dry Porasil C. This is the region for Porasil C which meets the criteria for accurate estimation of the surface area. The data are summarized in Table XVIII A. The standard deviation averages about 2% of the $\underline{K_A}$ values, about 5% of the $\underline{K_L}$ values for the normal alkanes. These values agree within experimental error with the values obtained on Porasil B wetted with 0.40 to 0.57 wt/wt H2O/ dry Porasil B.

Table XVIII B contains the $\underline{K_L}$ values that are obtained by using a least squares fit on the $\underline{V_{gs}}^{T}$ data for Chromosorb W in the region from 0.101 to 1.40 wt/wt H_2O/dry Chromosorb W. Because the liquid surface area is too small to be measured directly it is presumed to be proportional to the retention of the normal alkanes. The $\underline{K_L}$ values have standard deviations which average less than 2% of their magnitude. Using the $\underline{K_A}$ values of alkanes on Porasil C to define the surface area yields the $\underline{K_A}$ values of the halomethanes on Chromosorb W. However, because the effect is so small (the surface area ranges from 0.4 to 0.9 m^2/g), the standard deviations average more than 50% of the $\underline{K_A}$ values and therefore the latter are not reported.

The differences found in the $\underline{K_L}$ values for compounds absorbed by water adsorbed on Porasil C compared to those found using the water-Chromosorb W system are too large to be explained by experimental error, especially for $CHCl_3$ and CCl_4. The difference implies that the water on Porasil B and C is modified by the adsorbent. The mechanism of this modification has not been established, but there are two reasonable interpretations. Either the water is being oriented by the silica surface or the silica surface is being partially dissolved by the water. The latter has been proposed to

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TABLE XVIII

Adsorption and Absorption Equilibrium Constants for Compounds Sorbed by Water on Porasil C and on Chromosorb W at 25.0 °C

Compound	$\underline{K}_{\underline{A}}$	$\underline{K}_{\underline{L}}$
A. Porasil C		
CHF_3	0.0234	0.28
CH_3Cl	0.0708	3.1
CH_3Br	0.114	4.8
CH_2Cl_2	0.332	12.7
$CHCl_3$	0.580	9.9
CCl_4	0.280	2.1
C_4	0.0420	---
C_5	0.0936	0.27
C_6	0.216	0.73
C_7	0.501	1.8
C_8	1.17	4.2
B. Chromosorb W		
CH_3Cl	---	2.50
CH_3Br	---	3.65
CH_2Cl_2	---	9.58
$CHCl_3$	---	5.79
CCl_4	---	0.467

explain the formation of anomalous water.[48] The orientation argument is favored by the fact that the modified $\underline{K}_{\underline{L}}$ values appear to occur at surface areas greater than 1 m^2/g, i.e., where forces exist which cause the water surface to conform to the support surface. That the dissolution of silica also is a possibility is shown by the fact that surface areas of the dry Porasils (as measured by the BET method) changed after being treated with water.

The one definite conclusion from a comparison of the data for Porasil with that for Chromosorb W is that extreme care in the selection of the support material is necessary if a liquid is to be characterized as a bulk liquid. Indeed Guillemin, et al.,[49] consider liquid coatings on Spherosil (the European name for Porasil) to be best characterized as a form of modified gas-solid chromatography. They also note that the thermal stability of the modified supports is much higher than that normally associated with the coating liquid, which, they contend, proves that bonding between the liquid layer and the silica surface is particularly strong.

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CONCLUSIONS

The goal of the present discussion has been to revive and stimulate interest in gas-solid chromatography. By the use of sensitive detectors and surface modification of adsorbents highly selective and efficient separations are possible. Not only does the selectivity of gas-solid chromatography surpass that of gas-liquid chromatography, it also provides a more rational and quantitative basis for the prediction of retention volumes.

The use of surface modification provides a convenient means of attaining a more homogeneous surface. Also, because of specific interactions with the coating salt, additional selectivity is gained by appropriate choice of the coating salt. This is analogous to selective liquid phases in gas liquid chromatography, but has the added advantage that there are no "bleeding" problems.

The utility of gas-solid chromatography extends beyond analytical chemistry. As the preceding sections have illustrated, it can be a convenient means for studying the physical and chemical properties of surfaces, gas-solid interactions, and gas-solid inorganic complexes. This leads to the conclusion that gas-solid chromatography should be an especially effective method for characterizing catalysts and other solid-state materials. Another recent extension has been a study of the interactions of halogenated hydrocarbons (used as fumigants) with soils.[50]

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