

INVESTIGATION OF THE ADSORBENT BEHAVIOR OF THE ISOMERIC PHTHALIC ACIDS AND A PAIR OF THEIR POTASSIUM SALTS BY GAS-SOLID CHROMATOGRAPHY

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Adsorbents used in the past for gas-solid chromatography have included charcoal, silica gel, alumina, and molecular sieves. They have been used primarily for the analysis of permanent gases and non-polar compounds^{1,2}. More recently, chemically and physically modified adsorbents³, eutectic mixtures⁴, and inorganic salts⁵ have been used. However, investigation and utilization of specific interactions between adsorbates and adsorbents have been rather limited^{6,7} though they have recently gained more attention. DUFFIELD AND ROGERS⁸ reported separations of olefins by silver nitrate alone and SCOTT⁹ showed increased separation of saturated and unsaturated hydrocarbons when the solid coating on alumina was changed from NaCl → NaBr → NaI. ALTENAU AND ROGERS^{10,11} used various volatile organic compounds to study the adsorption behavior of some heavy-metal salts and found a variety of selective interactions.

The purpose of the present work was to investigate changes in adsorbent behavior with systematic variations both in chemical composition and in the position of the functional group in an attempt to elucidate separation behavior. The adsorbents studied were phthalic anhydride, phthalic acid, isophthalic acid, terephthalic acid, potassium acid phthalate, and dipotassium phthalate.

EXPERIMENTAL

Apparatus

Aerograph Models 600 and 660 gas chromatographs (Wilkins Instrument Co.) with flame-ionization detectors were used. The Model 600 was equipped with isothermal temperature control and external differential flow control; the Model 660 was equipped with proportional isothermal temperature control and internal differential flow control. Column-temperature indicators were calibrated using a Technique Associates Pyrometer. An Aerograph Model 650 Hydrogen Generator (Wilkins Instrument Co.) and a Speedomax H recorder (Leeds and Northrup Co.), with a chart speed of ½ in. per min and a sensitivity of 1 mV for a full-scale deflection, were used. A Speed Servo recorder (Esterline Angus Instrument Co.) with variable speeds and sensitivity was used to record data for Van Deemter plots.

Equipment for supporting studies included a Differential Thermal Analyzer Model 900 (E. I. duPont de Nemours and Co., Inc.) and Perkin-Elmer Model 221 infrared spectrophotometer.

Reagents

Organic adsorbates, obtained from a variety of vendors, were usually of the highest purity commercially available. A few technical grade preparations had very small impurity peaks but these did not interfere.

Most adsorbents were commercially available as reagent materials: Phthalic acid (Matheson-Coleman-Bell), phthalic anhydride, isophthalic acid, terephthalic acid (all from Eastman Organic Chemicals) and potassium hydrogen phthalate (J. T. Baker Co.). Dipotassium phthalate was prepared by adding aqueous 10 *N* potassium hydroxide to a 1.0 l solution (aqueous) containing 100 g of potassium acid phthalate until a pH of 7 was obtained. (Analysis—*theoretical*: C, 39.67 %; H, 1.65 %; K, 32.28 %; *found*: C, 39.53 %; H, 1.78 %; K, 32.50 %).

The carrier gas was Linde H. P. nitrogen that had been passed through a column of Linde Molecular Sieve 5A (30–50 mesh, 1/2 in. O.D., 30 cm long). The sieve was regenerated each time the nitrogen cylinder was replaced.

Procedures

Chromatographic columns were prepared by grinding, sieving, and collecting the 60/80 mesh fraction. Columns of 1/8 in. O.D. stainless steel tubing were packed by gently tapping the side or end. Vigorous vibration was avoided so as to minimize fragmentation of particles within the column. The 20 cm, 40 cm and 200 cm columns contained, respectively, about 0.5, 1.0 and 5.0 g of adsorbent. At least two different samples of each adsorbent, except the dipotassium salt, were studied.

Chromatographic samples were injected using the following techniques. Liquid was drawn into, then ejected from, a 10 μ l Hamilton syringe. The syringe was pumped in the air several times until an injection of approximately 1 μ l gave a deflection of 50–100 % of full scale at an attenuation of approximately X2 (input sensitivity at 10, output attenuation at 2). Alternatively, the vapor above the liquid was treated in the same way.

Flow rates were measured at the column outlet and at room temperature using a soap-bubble flow meter.

Retention times (t_r), measured with a stopwatch, have been reported only to the nearest 0.5 sec even though averages of three or more were often reproducible to 0.2 sec. When a short retention time made it essential to record to the nearest 0.1 sec, a large number of individual values of t_r were averaged. When the retention time did not change significantly with sample size, the time was recorded for deflections 50 % of scale or greater at an instrument attenuation of X10. When retention time changed with sample size, times were recorded at 50–55 % of full scale or were interpolated from values at other nearby percentages. The average sample was estimated to be about 1 μ g but when very short (or very long) retention times were involved, samples were probably at least a factor of ten smaller (or larger) than the average.

Capacity ratio (k) was calculated from the equation

$$k = t_r/t_m - 1$$

where t_m was the retention time for methane which was assumed not to adsorb significantly.

Surface area measurements were made by the method of NELSEN AND EGGERTSEN¹² using standards calibrated by the BET method. The surface areas of the samples

in m²/g were: phthalic anhydride, 0.18; phthalic acid, 0.07; isophthalic acid, 0.46; terephthalic acid, 8.84; potassium acid phthalate, 0.12; and dipotassium phthalate, 0.35.

Heats of adsorption were calculated only for temperature ranges where the slope of $\log K$ vs. $1/T$ was constant. The best straight line was estimated using the "least squares method" and the standard error of the slope was determined by regression analysis. The smaller the asymmetry of the peak and the smaller the dependence of its retention time on sample size, the higher was the confidence that one could place on comparisons involving the heats of adsorption.

RESULTS

Preliminary studies

Thermal stabilities of the adsorbents. Before columns of phthalic, isophthalic, or terephthalic acids had been heated to 100°, only the most volatile compounds could be eluted at room temperature. After the columns had been heated to 100°, the elution temperature of the various compounds listed in Tables I–III could be lowered.

TABLE I

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 200 CM PHTHALIC ACID COLUMN

Flow rate: at 39° 14.3 ml/min; at 50° and 60° 14.2 ml/min.

Compound	39°		50°		60°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Methane	24.5	—	25.0	—	25.5	—
Hexane	26.5	—1.088	26.5	—1.222	26.8	—1.293
Heptane	30.5	—0.613	29.0	—0.745	29.0	—0.863
Octane	42.5	—0.134	38.5	—0.268	35.0	—0.430
1-Hexene	26.7	—1.047	26.7	—1.168	26.8	—1.293
1-Heptene	31.0	—0.577	30.0	—0.699	29.0	—0.863
1-Octene	43.5	—0.111	38.5	—0.268	34.5	—0.452
Benzene	30.0	—0.650	29.0	—0.796	28.5	—0.928
Toluene	41.0	—0.172	36.5	—0.337	34.0	—0.478
Ethylbenzene	63.0	0.196	51.5	0.025	45.0	—0.116
Cyclohexene	27.0	—0.991	27.0	—1.099	27.0	—1.231
Cycloheptene	31.5	—0.544	30.0	—0.699	29.0	—0.863
Cyclooctene	43.0	—0.122	37.0	—0.319	34.0	—0.478
Cyclohexane	27.0	—0.991	27.0	—1.099	27.0	—1.231
Cycloheptane	31.0	—0.577	30.0	—0.699	29.5	—0.807
Cyclooctane	43.0	—0.122	38.5	—0.268	34.5	—0.452
Dichloromethane	26.0	—1.213	26.0	—1.398	26.3	—1.504
Chloroform	27.0	—0.991	26.7	—1.168	26.5	—1.407
Carbon tetrachloride	26.5	—1.188	26.2	—1.319	26.3	—1.504
Ethyl ether	31.0	—0.577	29.5	—0.745	28.5	—0.928
<i>n</i> -Propyl ether	53.5	0.085	48.5	—0.027	46.0	—0.095
<i>n</i> -Butyl ether	155	0.727	151	0.702	145	0.670
Acetone	31.5	—0.544	30.5	—0.658	30.0	—0.754
2-Butanone	40.0	—0.199	37.5	—0.302	36.0	—0.387
3-Pentanone	53.0	0.064	49.5	—0.009	47.5	—0.064
Methanol	32.0	—0.514	31.5	—0.585	31.0	—0.666
Ethanol	40.5	—0.185	39.5	—0.237	38.0	—0.310
<i>n</i> -Propanol	70.5	0.274	61.5	0.164	56.5	0.086
Ethyl acetate	45.0	—0.077	40.5	—0.208	37.5	—0.327
<i>n</i> -Propyl acetate	77.0	0.330	65.5	0.204	58.5	0.111
<i>n</i> -Butyl acetate	149	0.706	129	0.619	112	0.530

TABLE II

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 200 CM ISOPHTHALIC ACID COLUMN

Flow rate: at 50° 15.0 ml/min; at 75° 15.1 ml/min; at 100° 13.8 ml/min.

Compound	50°		75°		100°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Methane	23.0	—	22.5	—	24.5	—
Hexane	30.0	-0.517	26.0	-0.807	26.5	-1.088
Heptane	46.0	0.000	31.5	-0.398	28.6	-0.777
Octane	90.0	0.464	45.5	0.009	33.2	-0.456
1-Hexene	30.0	-0.517	26.0	-0.807	26.5	-1.088
1-Heptene	46.0	0.000	31.5	-0.398	28.8	-0.757
1-Octene	90.0	0.464	46.0	0.017	33.5	-0.432
Benzene	30.5	-0.487	26.5	-0.750	27.0	-0.991
Toluene	48.0	0.037	33.0	-0.331	29.5	-0.690
Ethylbenzene	88.0	0.452	47.0	0.033	34.0	-0.412
Cyclohexene	30.0	-0.517	25.5	-0.876	26.0	-1.213
Cycloheptene	46.0	0.000	30.5	-0.449	28.0	-0.845
Cyclooctene	88.0	0.452	41.5	-0.074	32.0	-0.514
Cyclohexane	28.0	-0.664	25.0	-0.955	26.0	-1.213
Cycloheptane	43.0	-0.061	30.0	-0.478	28.0	-0.845
Cyclooctane	86.0	0.438	41.0	-0.085	32.0	-0.514
Dichloromethane	26.5	-0.818	24.2	-1.122	25.4	-1.435
Chloroform	28.5	-0.622	24.8	-0.991	25.6	-1.349
Carbon tetrachloride	28.5	-0.622	24.8	-0.991	25.7	-1.311
Ethyl ether	48.0	0.037	29.5	-0.507	27.0	-0.991
<i>n</i> -Propyl ether	130	0.667	47.0	0.037	32.5	-0.487
<i>n</i> -Butyl ether	540	1.352	138	0.710	59.0	0.149
Acetone	53.5	0.124	31.5	-0.398	28.0	-0.845
2-Butanone	82.0	0.408	38.0	-0.162	30.0	-0.650
3-Pentanone	140	0.707	51.0	0.104	34.5	-0.390
Methanol	44.0	-0.040	29.5	-0.507	28.0	-0.845
Ethanol	75.0	0.354	41.0	-0.085	33.5	-0.435
<i>n</i> -Propanol	143	0.718	62.0	0.245	42.0	-0.146
Ethyl acetate	85.0	0.431	39.0	-0.135	30.5	-0.611
<i>n</i> -Propyl acetate	165	0.790	59.0	0.209	37.5	-0.275
<i>n</i> -Butyl acetate	450	1.269	120.0	0.636	55.0	0.093

Possible causes of the surface modification appeared to be: (a) loss or gain of adsorbed water, (b) conversion of acid to anhydride, (c) gain of volatile impurities other than water from the carrier gas, and (d) decrease in the capacity of the adsorbent. Each of the potential causes was ruled out except a decrease in adsorbent capacity.

First, loss or gain of adsorbed water was ruled out when injections of water and use of moist carrier gas for 12 h produced no significant changes in retention behavior of isophthalic and phthalic acids, respectively.

The second possibility, anhydride formation on the surface or an irreversible phase transition, could not be detected by differential thermal analysis or infrared spectroscopy. Furthermore, gas chromatographic evaluation of a 20 cm phthalic acid column, both before and after heating to 100°, showed an identical elution order, but lower values of the capacity ratios after heating, without a reversal of ketones and ethers to give the order found for the anhydride.

The possibility of gaining volatile impurities from the carrier gas was tested

TABLE III

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 200 CM TEREPHTHALIC ACID COLUMN

Flow rate: at 50° 29.1 ml/min; at 75° 27.2 ml/min; at 100° 26.0 ml/min; at 115° 27.8 ml/min; at 130° 25.7 ml/min.

Compound	50°		75°		100°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Methane	20.5	—	22.0	—	23.0	—
Hexane	45.0	0.079	32.5	-0.319	30.0	-0.602
Heptane	98.5	0.580	49.0	0.090	35.5	-0.267
Octane	275	1.094	92.5	0.505	50.5	0.077
1-Hexene	59.5	0.279	36.5	-0.180	30.0	-0.509
1-Heptene	140.5	0.767	61.0	0.248	38.0	-0.180
1-Octene	376	1.239	121.5	0.655	56.5	0.164
Benzene	67.0	0.356	41.0	-0.046	32.0	-0.398
Toluene	186.0	0.907	76.5	0.392	44.5	-0.033
Ethylbenzene	501	1.370	146	0.750	66.0	0.272
Cyclohexene	59.0	0.274	36.5	-0.181	29.5	-0.549
Cycloheptene	128	0.720	58.5	0.220	39.0	-0.159
Cyclooctene	275	1.094	105.5	0.580	54.0	0.130
Cyclohexane	41.0	0.000	30.5	-0.414	27.0	-0.760
Cycloheptane	82.0	0.477	45.0	0.017	33.5	-0.341
Cyclooctane	193	0.925	78.0	0.405	45.5	-0.010
Dichloromethane	39.5	-0.033	29.0	-0.498	26.0	-0.878
Chloroform	53.5	0.207	34.0	-0.264	28.0	-0.638
Carbon tetrachloride	41.0	0.000	31.0	-0.388	27.5	-0.732
Ethyl ether	101	0.530	65.0	0.262	44.0	-0.040
<i>n</i> -Propyl ether	310	1.096	165	0.790	90.0	0.463
<i>n</i> -Butyl ether	1275	1.734	552	1.362	255	1.003
Acetone	250	0.994	134	0.684	83.0	0.417
2-Butanone	429	1.247	217	0.926	125	0.646
3-Pentanone	707	1.473	356	1.161	184	0.845
Methanol	n.p.	n.p.	n.p.	n.p.		
Ethanol	187	0.852	115	0.602	70.0	0.310
<i>n</i> -Propanol	410	1.226	227	0.948	121	0.629
<i>n</i> -Butanol	971	1.617	492	1.309	235	0.965
Ethyl acetate	402	1.217	115	0.602	112	0.588
<i>n</i> -Propyl acetate	850	1.556	228	0.950	197	0.879
<i>n</i> -Butyl acetate	n.p.	n.p.	n.p.	n.p.	384	1.196

by heating the columns at 100°, without carrier gas flow, and finding the same alteration of adsorption behavior.

Evidence that a decrease in capacity of the adsorbent had occurred was shown by direct measurement of the change in surface area, S . However, as will be discussed later, plots of $\log K/S$ vs. boiling point probably did not coincide because the surfaces accessible to nitrogen and to the adsorbates were not exactly the same.

After prolonged heating at 100°, phthalic anhydride, at 39°, retained polar compounds more strongly, and plots of $\log K$ vs. boiling point were more nearly linear than before heating to drive off adsorbed water (and some anhydride.) Polar compounds were retained somewhat longer on the dried adsorbent than on the undried adsorbent whereas non-polar compounds appeared to be unaffected.

Columns of potassium acid phthalate did not undergo any alteration in adsorption behavior as a result of heating at 100° with the injection-port temperature

below 125°. However, a single column of potassium acid phthalate, after prolonged heating at 100° with an injection-port temperature greater than 135°, exhibited a drastic decrease in K values for hydrocarbons, presumably due to decomposition to the anhydride and the dipotassium salt¹³.

Dipotassium phthalate did not show any indication of alternation of retention properties upon continuous heating at 100° for six days.

Resolution. The degree of separation of a mixture of hexane, heptane and octane was investigated under essentially the same operating conditions, and observed to vary from adsorbent to adsorbent (Fig. 1). The excellent results for the terephthalic

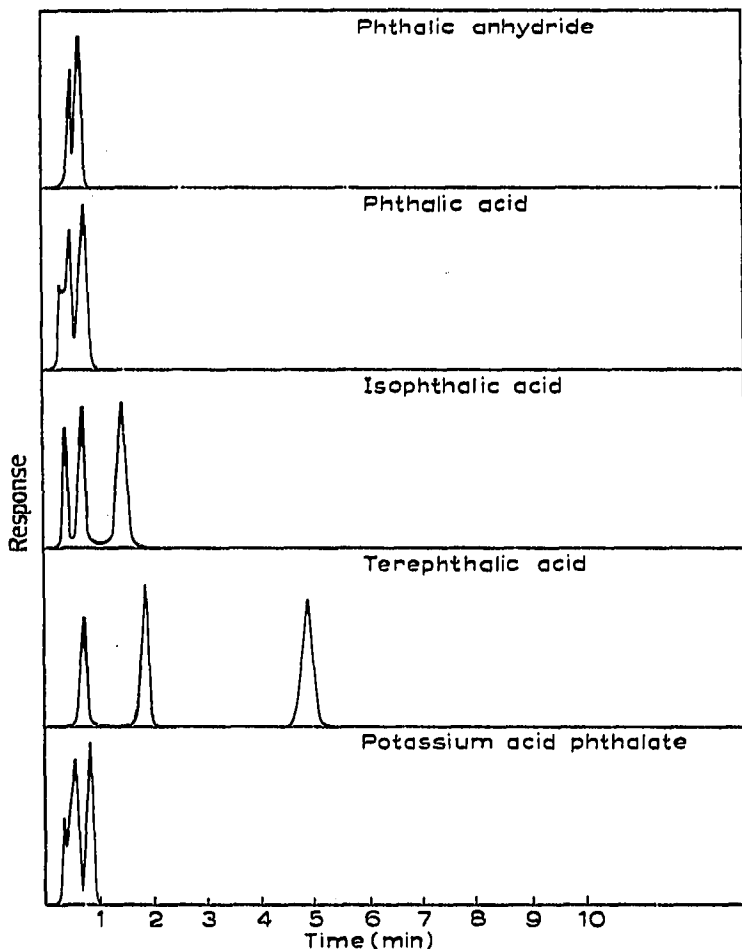


Fig. 1. Comparison of the separation of a hexane-heptane-octane mixture on 2 m columns at 50°.

acid probably reflects its much larger (20X) specific surface area compared to the next largest (isophthalic acid). Van Deemter plots for heptane and cycloheptane on isophthalic acid at 50° showed a minimum at a flow rate of 5 ml/min and gave HETP values of 21.5 mm for heptane and 26.5 mm for cycloheptane. Other adsorbents were assumed to be similar in characteristics.

Capacity ratios

Boiling-point plots. Figs. 2-5 illustrate some of the elution data in Tables I-IV for the isomeric phthalic acids and phthalic anhydride. The lines for hydrocarbon

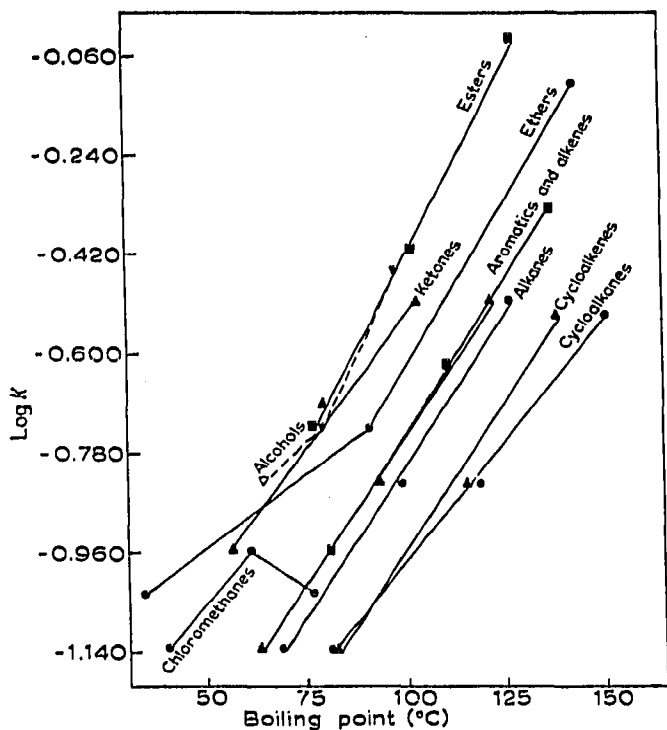


Fig. 2. Elution from phthalic anhydride at 50°.

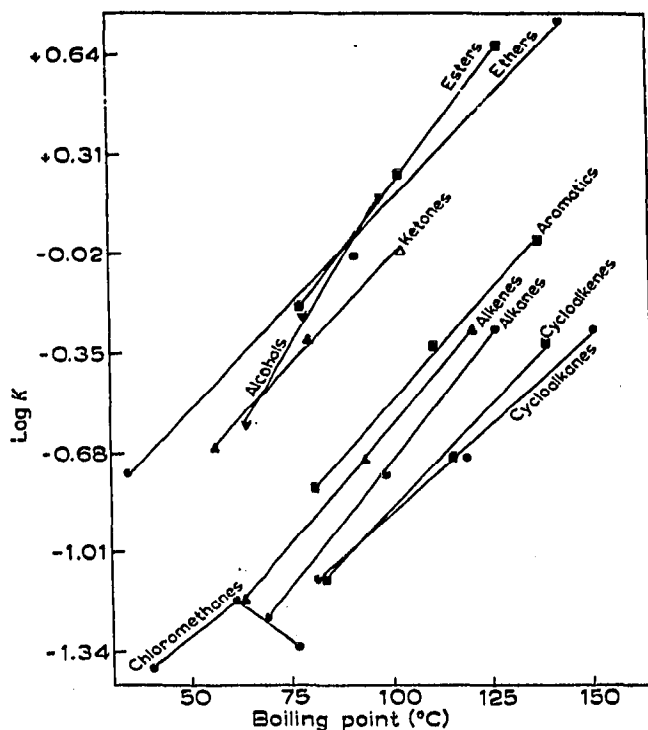


Fig. 3. Elution from phthalic acid at 50°.

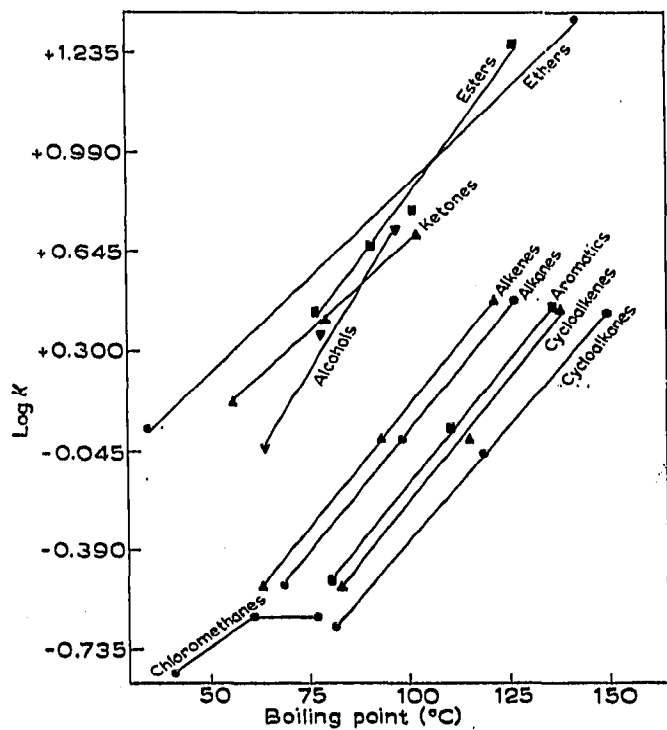


Fig. 4. Elution from isophthalic acid at 50°.

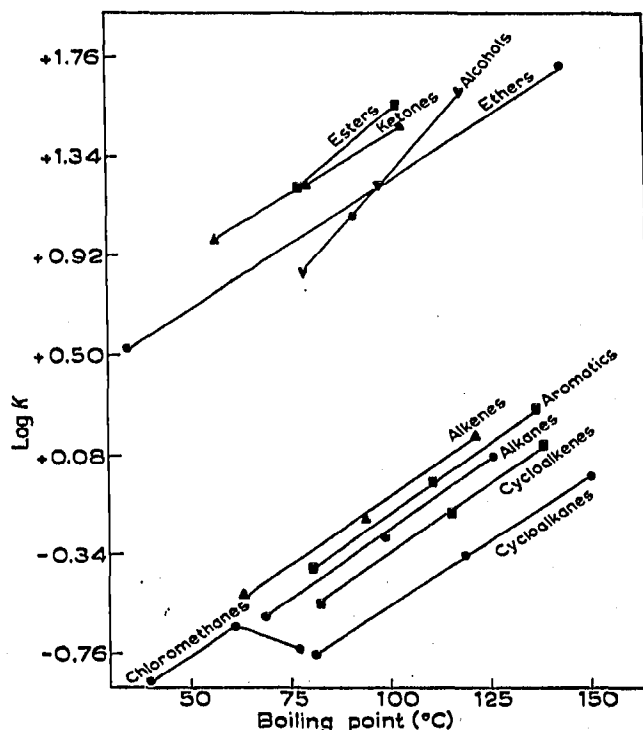


Fig. 5. Elution from terephthalic acid at 100°.

TABLE IV

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 200 CM PHTHALIC ANHYDRIDE COLUMN

Flow rate: at 39° and 50° 10.3 ml/min; at 60° 10.7 ml/min.

Compound	39°		50°		60°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Methane	27.0	—	27.0	—	26.5	—
Hexane	29.5	—1.034	29.0	—1.131	28.1	—1.220
Heptane	32.0	—0.733	31.0	—0.830	29.5	—0.947
Octane	38.5	—0.371	35.5	—0.502	32.5	—0.646
1-Hexene	29.5	—1.034	29.0	—1.131	28.1	—1.220
1-Heptene	32.5	—0.690	31.0	—0.830	29.5	—0.947
1-Octene	39.5	—0.334	35.5	—0.502	32.0	—0.646
Benzene	31.5	—0.777	30.0	—0.955	28.6	—1.101
Toluene	37.0	—0.431	33.5	—0.618	31.0	—0.770
Ethylbenzene	48.0	—0.109	39.5	—0.334	34.5	—0.541
Cyclohexene	29.5	—1.034	29.0	—1.131	28.0	—1.247
Cycloheptene	32.5	—0.690	31.0	—0.830	29.5	—0.947
Cyclooctene	39.0	—0.353	35.0	—0.529	31.5	—0.724
Cyclohexane	29.5	—1.034	29.0	—1.131	28.0	—1.247
Cycloheptane	32.5	—0.690	31.0	—0.830	29.5	—0.947
Cyclooctane	39.5	—0.334	35.0	—0.529	32.0	—0.682
Dichloromethane	29.8	—0.983	29.0	—1.131	28.0	—1.247
Chloroform	31.0	—0.830	30.0	—0.955	28.8	—1.062
Carbon tetrachloride	30.0	—0.955	29.5	—1.034	28.8	—1.062
Ethyl ether	30.0	—0.955	29.5	—1.034	28.5	—1.123
<i>n</i> -Propyl ether	34.5	—0.556	32.0	—0.733	30.0	—0.879
<i>n</i> -Butyl ether	64.0	0.137	48.0	—0.109	40.0	—0.293
Acetone	32.0	—0.733	30.0	—0.955	28.5	—1.123
2-Butanone	35.5	—0.502	32.5	—0.690	30.0	—0.879
3-Pentanone	40.5	—0.335	35.5	—0.503	32.5	—0.646
Methanol	32.5	—0.690	31.0	—0.830	29.5	—0.947
Ethanol	34.0	—0.587	32.0	—0.733	30.0	—0.879
<i>n</i> -Propanol	41.0	—0.286	36.5	—0.454	33.0	—0.611
Ethyl acetate	35.0	—0.529	32.0	—0.733	30.0	—0.879
<i>n</i> -Propyl acetate	43.5	—0.214	37.5	—0.411	33.0	—0.611
<i>n</i> -Butyl acetate	70.0	0.201	50.5	—0.060	41.0	—0.262

homologs were nearly parallel, and the relative positions of the lines for all compounds remained essentially constant with changes in column temperature. These adsorbents behaved like many partitioning liquids in that the lines for aromatics fell above those for the alkenes which, in turn, were above those for the alkanes. However, the order of the different hydrocarbon types on the individual columns showed different degrees of overlap of the cyclics, *i.e.*, aromatics, cycloalkenes and cycloalkanes, relative to the straight-chain alkenes and alkanes. Although the position of aromatics varied, they, too, preceded straight-chain alkanes using the isophthalic acid column.

Lines for oxygen-containing compounds crossed one another, so broad generalizations applicable to all the members of a homologous series cannot be stated. However, lines for the ethers and ketones were essentially parallel, except on phthalic anhydride. On terephthalic acid, ketones fell above ethers, while on phthalic acid and isophthalic acid the opposite was true.

Figs. 6–8 (and Tables V and VI) show the elution orders on potassium acid phthalate and dipotassium phthalate. Lines for the cycloalkenes and cycloalkanes

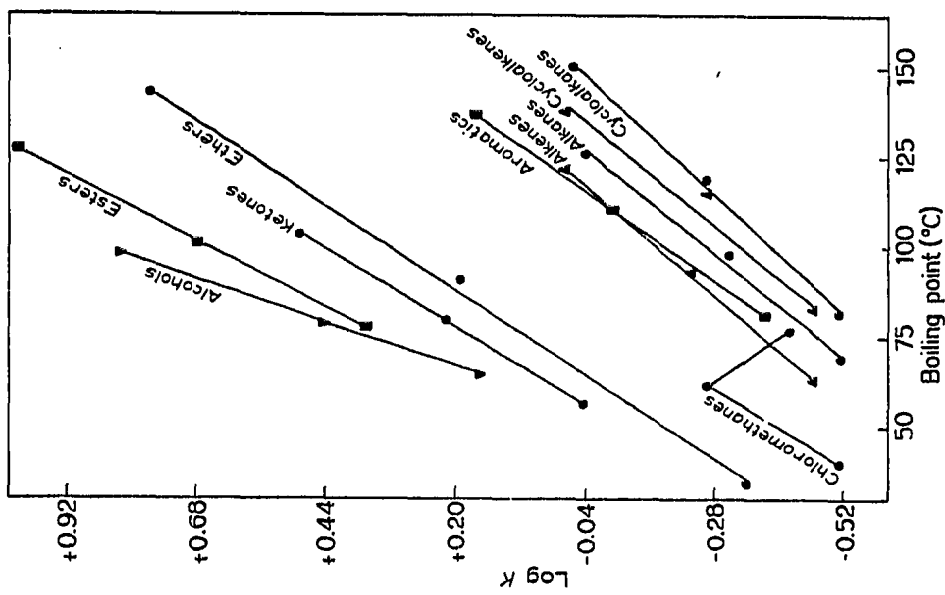


Fig. 8. Elution from dipotassium phthalate at 50°.

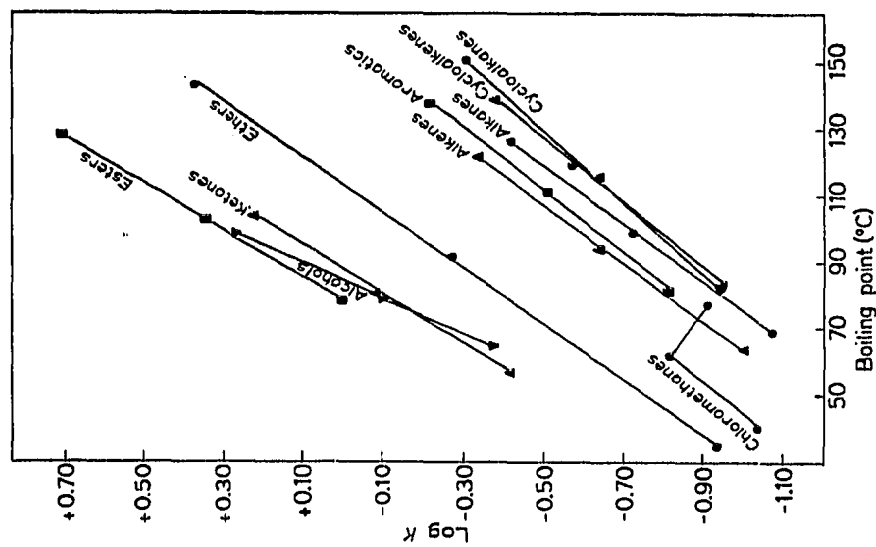


Fig. 7. Elution from potassium acid phthalate at 75°.

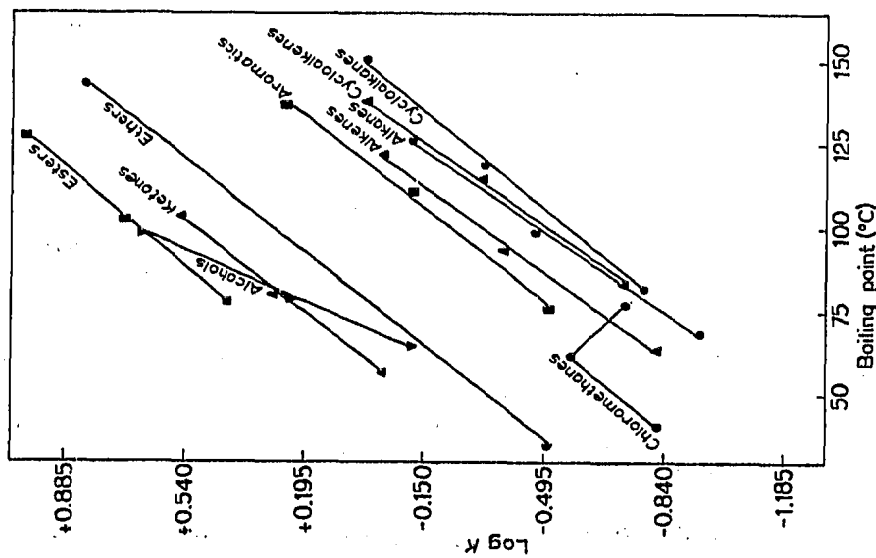


Fig. 6. Elution from potassium acid phthalate at 50°.

TABLE V

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 40 CM POTASSIUM ACID PHTHALATE COLUMN

Flow rate at all temperatures: 5.6 ml/min.

Compound	35°		50°		75°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Methane	13.0	—	13.0	—	13.0	—
Hexane	15.5	—0.717	14.5	—0.939	14.1	—1.073
Heptane	20.0	—0.269	17.5	—0.461	15.5	—0.717
Octane	32.0	0.164	23.0	—0.114	18.0	—0.415
1-Hexene	16.0	—0.636	15.0	—0.812	14.3	—1.000
1-Heptene	21.5	—0.184	18.5	—0.374	16.0	—0.636
1-Octene	35.5	0.238	25.0	—0.035	19.0	—0.335
Benzene	19.0	—0.335	17.0	—0.511	15.0	—0.812
Toluene	31.0	0.140	23.0	—0.114	17.0	—0.511
Ethylbenzene	57.5	0.534	36.0	0.248	21.0	—0.211
Cyclohexene	16.5	—0.570	15.5	—0.717	14.5	—0.939
Cycloheptene	22.5	—0.136	19.0	—0.335	16.0	—0.636
Cyclooctene	39.0	0.301	26.5	0.017	18.5	—0.374
Cyclohexane	16.0	—0.636	15.2	—0.772	14.5	—0.939
Cycloheptane	22.0	—0.160	19.0	—0.335	16.5	—0.570
Cyclooctane	37.5	0.274	26.5	0.017	19.5	—0.301
Dichloromethane	15.5	—0.717	15.0	—0.812	14.2	—1.036
Chloroform	17.5	—0.461	16.5	—0.570	15.0	—0.812
Carbon tetrachloride	16.5	—0.570	15.5	—0.717	14.6	—0.910

Compound	50°		60°		75°	
	t_r	$\log K$	t_r	$\log K$	t_r	$\log K$
Ethyl ether	16.5	—0.570	15.5	—0.717	14.5	—0.939
n-Propyl ether	31.5	0.152	25.0	—0.035	20.0	—0.269
n-Butyl ether	103	0.840	74.0	0.671	46.5	0.412
Acetone	25.0	—0.035	21.0	—0.211	18.0	—0.415
2-Butanone	37.5	0.274	30.0	0.117	24.0	—0.073
3-Pentanone	56.5	0.525	43.0	0.364	32.5	0.176
Methanol	23.0	—0.114	21.0	—0.211	18.5	—0.374
Ethanol	35.5	0.238	29.0	0.090	23.5	—0.093
n-Propanol	75.0	0.678	56.0	0.520	37.0	0.267
Ethyl acetate	47.0	0.418	35.0	0.228	26.0	0.000
n-Propyl acetate	79.0	0.706	58.0	0.539	42.0	0.348
n-Butyl acetate	143	1.000	109	0.868	80.0	0.712

fell below those for the straight-chain alkanes. Aromatics, however, were less consistent. On the dipotassium salt, they nearly coincided with straight chain alkenes throughout the temperature range studied, whereas on the monopotassium salt, they were above at 50° and below at 75°.

The lines for different homologous series of oxygen-containing compounds intersected but the order did not change noticeably with temperature. The overall pattern was quite similar to that for the acid adsorbents. Lines for the ethers and ketones were approximately parallel, but ketones were always more strongly retained than ethers.

Values "corrected" for differences in specific areas of adsorbents. KISELEV *et al.*¹⁴

TABLE VI

RETENTION TIMES AND LOG CAPACITY RATIOS FOR COMPOUNDS ELUTED FROM A 40 CM DIPOTASSIUM PHTHALATE COLUMN

Flow rate at all temperatures: 5.5 ml/min.

Compound	35°		50°		75°	
	<i>t_r</i>	log <i>K</i>	<i>t_r</i>	log <i>K</i>	<i>t_r</i>	log <i>K</i>
Methane	13.0	—	13.0	—	13.0	—
Hexane	19.0	—0.335	17.0	—0.511	15.5	—0.717
Heptane	24.0	—0.073	19.5	—0.301	16.5	—0.570
Octane	37.0	0.267	25.0	—0.035	18.5	—0.374
1-Hexene	19.0	—0.335	17.5	—0.461	16.0	—0.636
1-Heptene	25.5	—0.017	20.0	—0.238	17.0	—0.511
1-Octene	41.5	0.340	26.0	0.000	19.0	—0.335
Benzene	21.5	—0.184	18.5	—0.374	16.5	—0.570
Toluene	33.0	0.188	23.5	—0.093	18.0	—0.414
Ethylbenzene	55.0	0.348	32.0	0.164	21.0	—0.212
Cyclohexene	18.5	—0.374	17.5	—0.461	16.0	—0.636
Cycloheptene	24.0	—0.073	20.0	—0.269	17.0	—0.511
Cyclooctene	37.0	0.267	26.0	0.000	19.0	—0.335
Cyclohexane	18.0	—0.414	17.0	—0.511	16.0	—0.636
Cycloheptane	23.0	—0.114	20.0	—0.269	17.5	—0.461
Cyclooctane	34.5	0.218	25.5	—0.017	19.0	—0.335
Dichloromethane	19.0	—0.335	17.5	—0.461	16.0	—0.636
Chloroform	24.0	—0.073	20.0	—0.269	17.0	—0.511
Carbon tetrachloride	20.0	—0.269	18.0	—0.414	16.3	—0.595

	50°		60°		75°	
	<i>t_r</i>	log <i>K</i>	<i>t_r</i>	log <i>K</i>	<i>t_r</i>	log <i>K</i>
Ethyl ether	19.5	—0.301	18.0	—0.414	16.5	—0.570
<i>n</i> -Propyl ether	33.0	0.188	27.0	0.033	21.0	—0.212
<i>n</i> -Butyl ether	90.0	0.772	62.0	0.576	34.5	0.217
Acetone	25.0	—0.035	21.5	—0.184	19.0	—0.335
2-Butanone	34.5	0.217	28.5	0.075	21.5	—0.184
3-Pentanone	53.5	0.494	38.5	0.292	27.0	0.033
Methanol	32.0	0.164	31.0	0.140	22.5	—0.136
Ethanol	49.0	0.442	45.0	0.391	28.5	0.075
<i>n</i> -Propanol	100	0.825	88.0	0.761	50.5	0.459
Ethyl acetate	43.0	0.364	34.0	0.210	23.5	—0.093
<i>n</i> -Propyl acetate	75.0	0.678	55.0	0.509	34.0	0.210
<i>n</i> -Butyl acetate	150	1.022	101	0.831	56.0	0.520

working with different samples of wide-pore deactivated carbons showed that they could correct their retention data for differences in surface areas by dividing the capacity ratio, *K*, by the surface area, *S*. Such a procedure is more likely to be successful for comparisons of homogeneous surfaces having the same energies of the surface sites and for very similar adsorbates. As Fig. 9 shows, our attempted correction was not successful for a solid that undoubtedly had a wide energy distribution of its surface sites. Both the adsorbents and the adsorbates in the present study differed widely among themselves in terms of the different physical interactions that might dominate a particular situation^{15, 16}. The differences in surface-coverage histories of the widely diverse adsorbates as they passed through the columns in the present study

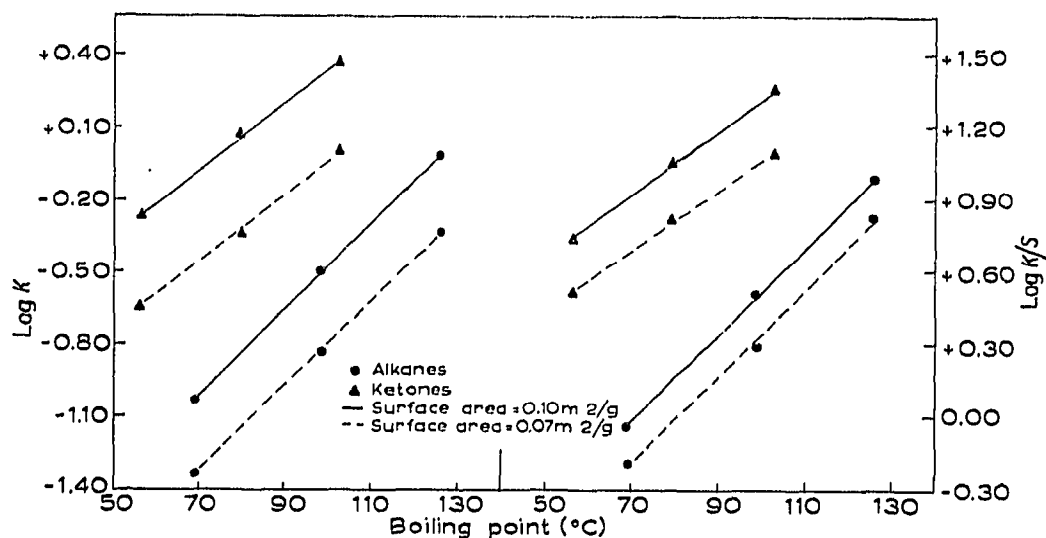


Fig. 9. Effect of surface area (S) of phthalic acid on retention as measured by $\log K$ and $\log K/S$.

would be much greater than the differences encountered by KISELEV *et al.*¹⁴. In going from one adsorbent to another, differences in pore-size distribution would be expected to add another uncertainty to a correction based upon surface areas measured with nitrogen. (Interpretations of values for heats and entropies of adsorption are, of course, subject to questioning on the same bases as the capacity ratios.)

In spite of those limitations, useful comparisons should be possible if one attempted to interpret only shifts in the relative order rather than the absolute values themselves. The $\log K/S$ values given in Table VII have been normalized to 60° and to $0.10 \text{ m}^2/\text{g}$ surface area. One adsorbate from each class of organic compounds studied is shown on each adsorbent. The adsorbents are arranged in the order of decreasing retention of *n*-octane. Ranges of $\log K/S$ for a given adsorbate on all adsorbents and for all adsorbates on a given adsorbent have also been shown.

TABLE VII

LOG K/S VALUES CALCULATED FOR 60° AND $0.100 \text{ m}^2/\text{g}$ FOR SELECTED ADSORBATES

Values underlined with a single line: disproportionately large values; a double line: disproportionately small value; and a dashed line: possibly too large or too small.

Adsorbate	KHP	Meta	Ortho	K_2P	Anhyd	Para	Total $\Delta \log K/S$
<i>n</i> -Octane	-0.16	-0.48	-0.59	-0.84	-0.99	-1.10	0.94
Cyclooctane	-0.04	-0.53	-0.61	-0.81	-1.02	-1.23	1.19
1-Octene	-0.08	-0.47	-0.61	-0.80	-0.99	-0.95	0.91
Cyclooctene	-0.07	-0.51	-0.64	-0.80	-1.06	-1.07	1.00
Benzene	-0.55	<u>-1.34</u>	-1.09	-1.13	-1.44	-1.76	1.21
Ethyl ether	-0.64	-0.93	-1.09	-1.08	-1.46	-0.61	0.82
Acetone	-0.13	-0.85	-0.91	-0.84	-1.46	0.00	1.46
Ethyl acetate	<u>+0.31</u>	-0.56	-0.49	-0.45	-1.22	+1.11	<u>2.33</u>
Ethanol	<u>+0.17</u>	-0.58	-0.47	-0.27	-1.18	-0.35	1.35
Total $\Delta \log K/S$	0.95	0.87	0.62	0.86	<u>0.47</u>	<u>2.87</u>	

Several points are immediately obvious from these data. First, among the adsorbates, ethyl acetate showed the greatest range of values; among the adsorbents, the *para* acid showed the greatest range (possibly due, in part, to its relatively large specific surface area) and the *ortho* anhydride, the smallest range. Hence, ethyl acetate should be especially useful for detecting and measuring differences between adsorbents; the *para* acid should be useful for detecting substances containing *n*-electrons and/or capable of hydrogen bonding. Oxygen-containing compounds were held up disproportionately long on the *para* acid and, except for the ether, on both of the potassium salts. Second, although nearly all of the values for benzene and ethyl ether look small on an absolute basis compared to the alkanes and alkenes, the differences can probably be ascribed to the higher boiling points of the latter. However, the retention value for benzene on the *meta* acid appears to be disproportionately small compared to cyclooctane. Since both are cyclic, an explanation based upon rejection of benzene by small pores does not seem adequate. Third, the monopotassium salt nearly always showed the greatest retention, probably due to the fact that it is polar, polarizable, and capable of both accepting and donating hydrogen to form hydrogen bonds. Fourth, the dipotassium salt was the only substance to show a significantly stronger retention of ethanol compared to other adsorbates.

Heats of adsorption

Before heats of adsorption are discussed, it should be noted that high temperatures and vacuum pretreatment, which are usually used to clean the surfaces of conventional inorganic solids, could not be used for the organic adsorbents because of volatility and/or decomposition. Consequently, one can expect that conditions other than those used in this study might alter the results, especially in the case of phthalic anhydride. Furthermore, it seemed expedient to use different column lengths so as to minimize the number of very short and very long retention times.

In principle, the standard error of the slope, S_b , might have been reduced either by increasing the temperature range over which the K values were measured or by significantly increasing the number of measurements. The former was precluded due to the volatility of the adsorbents, non-linearity of some $\log K$ vs. $1/T$ plots, and some very small retention times at higher temperatures. An increase in the number of replicates was impractical for the large number of adsorbates and adsorbents studied.

For hydrocarbons, ΔH values (Table VIII) for each adsorbent increased with increasing molecular weight within a homologous series. However, polar compounds were much less regular in their behavior. One series of adsorbates, the chloromethanes, followed a different pattern on going from one adsorbent to another.

The *para* acid, which had the highest specific surface area (and would, therefore, usually have the smallest fraction of its surface covered by adsorbate) consistently had the highest heats of adsorption. The *meta* acid, which had the next highest area, also had high heats of adsorption in most cases. One adsorbent, the *ortho* acid, showed a decrease (that was probably significant) in ΔH with an increase in chain length for each homologous series. Potassium acid phthalate showed similar behavior, but only with acetates and methyl ketones; phthalic anhydride showed a decrease of questionable significance for ketones. These changes emphasize the fact that a larger value of K does not necessarily result in a larger heat of adsorption, even within a given homologous series. Differences in entropy can also play a significant role.

TABLE VIII

HEATS OF ADSORPTION (kcal/mole)

All values are negative, i.e. exothermic; and the error reported is the standard error of the slope S_b .

Adsorbate	Phthalic anhydride	Phthalic acid	Isophthalic acid	Terephthalic acid	Potassium acid phthalate	Dipotassium phthalate
Hexane	4.26 ± 0.11	4.68 ± 0.83	6.21 ± 0.28	7.44 ± 0.31	4.15 ± 1.12	4.56 ± 0.34
Heptane	4.89 ± 0.26	5.72 ± 0.22	8.44 ± 0.34	9.24 ± 0.33	5.37 ± 0.21	5.93 ± 0.44
Octane	6.29 ± 0.17	6.77 ± 0.37	9.99 ± 0.61	11.10 ± 0.40	6.89 ± 0.68	7.64 ± 0.67
1-Hexene	4.26 ± 0.11	5.62 ± 0.06	6.21 ± 0.28	8.60 ± 0.34	4.33 ± 0.44	3.61 ± 0.10
1-Heptene	5.88 ± 0.30	6.54 ± 0.55	8.23 ± 0.21	10.31 ± 0.02	5.42 ± 0.16	5.90 ± 0.36
1-Octene	7.13 ± 0.32	7.80 ± 0.36	9.73 ± 0.54	11.71 ± 0.06	6.82 ± 0.64	8.00 ± 1.00
Benzene	7.41 ± 0.42	6.36 ± 0.19	5.48 ± 0.16	8.20 ± 0.14	5.76 ± 0.17	4.58 ± 0.51
Toluene	7.75 ± 0.46	7.00 ± 0.32	7.90 ± 0.38	10.24 ± 0.02	7.84 ± 0.05	7.18 ± 0.59
Ethylbenzene	9.88 ± 0.24	7.13 ± 0.40	9.37 ± 0.68	11.98 ± 0.24	8.98 ± 0.11	6.80 ± 0.51
Cyclohexene	4.87 ± 0.25	5.49 ± 0.32	7.56 ± 0.28	8.97 ± 0.06	4.44 ± 0.02	3.18 ± 0.22
Cycloheptene	5.88 ± 0.30	7.29 ± 0.12	9.19 ± 0.17	9.59 ± 0.23	6.02 ± 0.03	5.23 ± 0.32
Cyclooctene	8.48 ± 0.25	8.14 ± 0.50	10.52 ± 0.04	10.49 ± 0.18	8.09 ± 0.24	7.20 ± 0.40
Cyclohexane	4.87 ± 0.25	5.49 ± 0.32	5.97 ± 0.12	8.28 ± 0.03	3.62 ± 0.22	2.66 ± 0.13
Cycloheptane	5.88 ± 0.30	6.17 ± 0.71	8.53 ± 0.16	8.92 ± 0.15	4.91 ± 0.18	4.15 ± 0.25
Cyclooctane	7.96 ± 0.55	7.54 ± 0.50	10.37 ± 0.03	10.19 ± 0.10	6.87 ± 0.41	6.63 ± 0.23
Dichloromethane	6.04 ± 0.42	6.65 ± 0.04	6.69 ± 0.42	9.21 ± 0.04	3.89 ± 0.42	3.61 ± 0.10
Chloroform	5.30 ± 0.24	9.51 ± 0.82	7.90 ± 0.36	9.21 ± 0.11	4.28 ± 0.40	5.23 ± 0.32
Carbon tetrachloride	2.45 ± 0.67*	7.22 ± 0.71	7.50 ± 0.11	7.96 ± 0.16	4.07 ± 0.18	3.90 ± 0.22
Ethyl ether	3.84 ± 0.13	8.03 ± 0.20	11.18 ± 0.24	13.04 ± 0.45	7.36 ± 0.31	5.36 ± 0.09
n-Propyl ether	7.38 ± 0.41	4.11 ± 0.58	12.57 ± 0.04	14.48 ± 0.28	8.36 ± 0.10	7.99 ± 0.43
n-Butyl ether	9.83 ± 0.82	1.30 ± 0.09	13.09 ± 0.21	16.72 ± 0.19	8.54 ± 0.39	11.12 ± 1.03
Acetone	8.92 ± 0.71	4.80 ± 0.24	10.55 ± 0.11	13.20 ± 0.57	7.54 ± 0.25	5.94 ± 0.42
2-Butanone	8.62 ± 0.03	4.30 ± 0.24	11.52 ± 0.12	13.75 ± 0.54	6.89 ± 0.14	8.03 ± 0.74
3-Pentanone	7.89 ± 0.78	2.93 ± 0.24	11.95 ± 0.04	14.36 ± 0.08	6.92 ± 0.21	9.16 ± 0.06
Methanol	5.88 ± 0.30	3.48 ± 0.13	8.78 ± 0.33	n.c.**	5.20 ± 0.37	n.c.
Ethanol	6.68 ± 0.03	2.86 ± 0.28	8.60 ± 0.09	12.40 ± 0.55	6.58 ± 0.10	n.c.
n-Propanol	7.43 ± 0.15	4.30 ± 0.42	9.41 ± 0.02	13.65 ± 0.54	8.21 ± 0.47	n.c.
Ethyl acetate	8.00 ± 0.76	5.72 ± 0.16	11.35 ± 0.06	n.c.	8.30 ± 0.19	9.16 ± 1.02
n-Propyl acetate	9.08 ± 0.05	5.01 ± 0.44	11.60 ± 0.04	n.c.	7.10 ± 0.26	9.37 ± 0.79
n-Butyl acetate	10.59 ± 0.78	4.03 ± 0.03	12.80 ± 0.14	n.c.	5.72 ± 0.16	10.05 ± 0.62

* The lowest value of r^2 (fraction of the variation in log capacity ratio accounted for by variation in column temperature *via* a linear function) was 0.929, for carbon tetrachloride; r^2 values were usually greater than 0.990.** n.c. = heat of adsorption, not calculated since the slope of log K vs. $1/T$ was not linear.

Relative changes in entropies of adsorption

The limitations of using only entropy changes to determine the adsorption model¹⁷ or to explain the chromatographic separation process^{16,18} have been previously noted. Computation of entropy changes requires the adjustment of data to a standard or reference state. Such an adjustment was not feasible for elution data, as pointed out earlier, because the partial pressures of the adsorbates and the fractions of the surface covered were not accurately known and, moreover, they changed across the peak band at any instant and also with time as the peak progressed down the column. Comparisons of different adsorbates on a given column are probably more reliable than comparisons between columns for a given adsorbate.

Entropy changes were calculated assuming that the capacity ratio was directly proportional to the thermodynamic adsorption constant, K_a , in order to make relative, but not absolute, comparisons (Table IX). For a limited number of adsorbates, the relative entropy changes for non-polar compounds were roughly the same, and small changes, if significant, accompanied an increase in chain length. However, there were a few relatively large differences between related adsorbates on the same adsorbent (*e.g.*, ethyl ether and butyl ether eluted from phthalic acid) as well as relative changes on going from one adsorbent to another. In several of these cases, the more strongly retained compound had the smallest entropy change.

TABLE IX

ENTROPY CHANGES FOR SELECTED COMPOUNDS

Calculated using $\log K$ values at 50° except for the oxygen-containing adsorbates on terephthalic acid for which values at 75° were used. The entropy changes are in units of cal/deg.-mole.

Adsorbate	Phthalic anhydride	Phthalic acid	Isophthalic acid	Terephthalic acid	Potassium acid phthalate	Dipotassium phthalate
Octane	-21.7	-22.2	-30.9	-29.4	-21.8	-23.9
Octene	-24.4	-25.3	-30.1	-30.6	-21.2	-24.8
Ethylbenzene	-29.1	-18.8	-26.9	-30.5	-26.7	-20.3
Cyclooctene	-28.5	-26.7	-30.5	-27.2	-23.9	-22.3
Cyclooctane	-27.9	-27.6	-29.9	-27.5	-20.2	-21.1
Ethyl ether	-18.0	-28.3	-34.8	-32.8	-19.9	-18.2
<i>n</i> -Butyl ether	-30.7	-0.81	-33.3	-35.3	-22.6	-30.6
Acetone	-31.9	-17.7	-27.0	-34.0	-21.7	-19.9
3-Pentanone	-26.7	-9.17	-33.5	-32.6	-19.0	-26.1
Ethanol	-23.6	-9.93	-25.0	-29.9	-19.2	
Ethyl acetate	-23.1	-18.7	-33.1		-23.5	-26.4
<i>n</i> -Butyl acetate	-30.9	-15.3	-33.7		-10.0	-26.4

The present data also illustrate a problem that results from using the capacity ratio, rather than the adsorption constant, to obtain the change in free energy. In some cases, although the computed entropy changes were negative for all the adsorbates, the corresponding free energy changes were positive when the chromatographic reaction was low, *i.e.*, when $\log K$ was less than unity.

When comparing different adsorbents, the effect on the retention values of different crystal structures is an important question that arises. However, on the basis of the relatively small changes in ΔH that were observed for some of the same adsorbates when thallium(I) nitrate was changed from one crystal form to another¹⁹,

it appears that differences in crystal structures probably introduced only very small effects on the retention times.

Despite the relatively large uncertainties in the data, the results indicate that more thorough studies should be rewarding.

CONCLUSION

An investigation of adsorption behavior of phthalic anhydride, the isomeric phthalic acids and a pair of potassium salts showed that relatively small changes in chemical composition or in the position of the functional group resulted in large changes in chromatographic retention of organic adsorbates. Terephthalic acid, partly because of its very large specific surface area, exhibited the greatest range of $\log K/S$ values and also the highest heats of adsorption. Phthalic anhydride, which had an intermediate value of specific surface area, showed the smallest range of $\log K/S$ values. Among the adsorbates, ethyl acetate had the greatest range of $\log K/S$ values and should be the most useful for measuring changes in surface behavior.

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SUMMARY

Gas-solid chromatography was used to study differences in behavior of representative organic adsorbates on the isomeric *o*-, *m*-, and *p*-phthalic acids plus the anhydride, mono-, and di-potassium salts of the *ortho* acid. Plots of logarithm of the capacity ratio *vs.* boiling point were distinctly different for each adsorbent. Correction of capacity ratios for differences in surface area (nitrogen adsorption) was shown to be inadequate for this type of adsorbent. Even so, the differences were sometimes so great that they could be considered significant. Heats of adsorption and relative changes in entropy are reported.

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