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 model[17] 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
n-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
n-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 another[19],

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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