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# THE INTERACTION OF AROMATIC COMPOUNDS IN ALCOHOL SOLUTION WITH SEPHADEX LH-20 DEXTRAN

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## SUMMARY

The adsorption of aromatic molecules from methanol and isopropanol solutions by Sephadex LH-20 Dextran has been shown to be a function of $\pi$ bonding for hydrocarbons and a combination of $\pi$ and hydrogen bonding for substituted compounds and heterocycles. The adsorption values for planar aromatic hydrocarbons can be predicted from the resonance energies. The gel appears to function as both a soft and hard acid in PEARSON's terminology.

## INTRODUCTION

A recent publication[1] has suggested that the mechanism of adsorption for phenols, anilines and benzoic acid derivatives on Sephadex dextran gels is through hydrogen bonding. This conclusion is supported by the data except for halogen substituted compounds which appear to behave in an unusual manner. There also seems to be considerable scatter for alkyl substituted phenols on Sephadex LH-20 Dextran.

Several other studies[2,3] indicate that aromatic hydrocarbons are strongly adsorbed by these gels from isopropanol solutions. Since there is no possibility for hydrogen bonding here it would appear that other mechanisms must be working for adsorption besides hydrogen bonding. EAKER AND PORATH[4] have suggested $\pi$ bonding as a mechanism for the adsorption of aromatics on Sephadex G-10.

The present work was undertaken to determine if a correlation between the adsorption values for aromatic compounds and energies associated with the $\pi$ electron cloud of the compounds existed. If so, it would appear that at least part of the adsorption behavior could be associated with electron–gel interactions as well as hydrogen bonding.

## MATERIALS AND METHODS

The chromatographic column was a 0.5 cm I.D., 50 cm glass tube equipped with a stopcock at its outlet. Teflon and metal fittings connected the column to Teflon tubing through which the solvent was pumped. A peristaltic pump (Milton Roy mini

pump) provided a flow rate of about 1 ml/min. A Beckman DU spectrophotometer equipped with a variable space flow cell and connected to a Sargent SRL recorder served as the detection system most of the time, but on occasion a Waters R-4 differential refractometer was used.

The gel was Sephadex LH-20, 25–100 $\mu$ particle size. This gel is a partially alkylated cross-linked dextran. Methanol was used as the solvent and solutes were reagent grade as far as possible. All solutions were approximately 1%.

Samples (10, 25 and 50 $\mu$l) were injected directly into the column through a septum with a syringe. At least 3 elution values were obtained on all compounds.

The column was calibrated by the method previously described[5]. $V_0$ was determined using a 0.5% aqueous solution of Blue Dextran. $(V_0 + V_i)$ was taken as the elution volume of either acetone or hexane. These values were identical. Both $V_0$ and $(V_0 + V_i)$ were determined daily and showed little variation.

$K$ values were computed in the standard way*. The variability of the results was obtained by making multiple determinations of aniline and phenol constants over a period of several months. The standard deviation for 14 results on these two compounds was ± 0.07.

## RESULTS

$K$ values for methanol solutions of a group of planar aromatic hydrocarbons are listed in Table I. Elution values in isopropanol were taken from ref. 3. Resonance energies were obtained from ref. 6.

A least squares solution for absorption values vs. resonance energy indicates a linear correlation for the planar aromatic hydrocarbons. For methanol solutions the equation is:

$$K = 0.0199 \text{ (Res. Energy)} + 0.54 \tag{1}$$

The pooled value for the differences between experimental and calculated values is ± 0.08 which is nearly identical with the standard deviation of experimental results.

A least squares solution for OELERT's data in isopropanol[3] and resonance energies yields the equation:

$$V_s = 0.0158 \text{ (Res. Energy)} + 0.31 \tag{2}$$

Pooled error value is ± 0.10 units.

OELERT's values are not $K$ values but are numbers proportional to them since he assigned a $V_s$ value of 1.000 to benzene and then calculated all other $V_s$ values in relation to this.

Since the resonance energies are a measure of $\pi$ electron cloud densities of the hydrocarbons it appears that bonding of the hydrocarbons and gels takes place through the $\pi$ electron cloud and constitutes a Lewis acid–base complex. To be sure that this did not result from inadvertent contamination of the gel, the gel was subjected to spectrographic elemental UV analysis. Sodium and boron were found in about 100 p.p.m. concentrations, aluminum, iron and silicon were less than 10 p.p.m., and other metals less than 3 p.p.m.

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* $K = (V_e - V_0)/V_i$.

TABLE I

RESONANCE ENERGIES AND ADSORPTION VALUES FOR PLANAR AROMATIC HYDROCARBONS

| Compound | Res. energy[a] (kcal) | Adsorption value | | | | | |
|---|---|---|---|---|---|---|---|
| | | MeOH | | | iPrOH | | |
| | | Exp. | Calc. | $\Delta$ | Exp.[b] | Calc. | $\Delta$ |
| Benzene | 36.0 | 1.33 | 1.26 | 0.07 | 1.00 | 0.88 | 0.12 |
| Toluene | 35.4 | 1.33 | 1.24 | 0.09 | 0.96 | 0.87 | 0.09 |
| Ethylbenzene | 35.2 | — | — | — | 0.92 | 0.87 | 0.05 |
| Xylene | 34.8 | 1.28 | 1.23 | 0.05 | 0.95 | 0.86 | 0.09 |
| Naphthalene | 61.0 | 1.71 | 1.75 | —0.04 | 1.22 | 1.27 | —0.05 |
| 2-Methylnaphthalene | 59.4 | 1.66 | 1.72 | —0.06 | 1.18 | 1.25 | —0.07 |
| 2,6-Dimethylnaphthalene | 58.8 | 1.62 | 1.71 | —0.09 | 1.13 | 1.24 | —0.11 |
| Anthracene | 83.5 | 2.15 | 2.20 | —0.05 | 1.59 | 1.63 | —0.04 |
| Phenanthrene | 91.3 | 2.36 | 2.36 | 0.00 | 1.62 | 1.75 | —0.13 |
| Fluorene | 75.9 | 1.93 | 2.05 | —0.12 | 1.38 | 1.51 | —0.13 |
| Chrysene | 116.5 | 3.03 | 2.86 | 0.17 | 2.30 | 2.15 | 0.15 |

[a] Ref. 6.
[b] Ref. 3.

The $K$ values for a variety of other aromatic compounds for which resonance energies were available were also determined and results are given in Table II. $K$

TABLE II

RESONANCE ENERGIES AND ADSORPTION VALUES FOR VARIOUS AROMATIC COMPOUNDS

| Compound | Res. energy[a] (kcal) | Adsorption value | | | | | |
|---|---|---|---|---|---|---|---|
| | | MeOH | | | iPrOH | | |
| | | Exp. | Calc. | $\Delta$ | Exp.[b] | Calc. | $\Delta$ |
| Biphenyl | 71.0 | 1.62 | 1.95 | —0.33 | 1.23 | 1.43 | —0.20 |
| trans-Stilbene | 76.9 | 1.84 | 2.07 | —0.23 | 1.45 | 1.52 | —0.07 |
| 9,10-Dihydroanthracene | 72.2 | — | — | — | 0.98 | 1.45 | —0.47 |
| Benzophenone | 72 | — | — | — | 1.28 | 1.45 | —0.17 |
| Benzoic acid | 47 | 1.50 | 1.47 | 0.03 | 1.21 | 1.05 | 0.16 |
| Benzaldehyde | 35 | — | — | — | 1.21 | 0.86 | 0.34 |
| Acetophenone | 37 | — | — | — | 1.12 | 0.89 | 0.23 |
| Anisole | 36 | 1.46 | 1.26 | 0.20 | 1.13 | 0.88 | 0.25 |
| Phenol | 36 | 1.65 | 1.26 | 0.39 | 1.21 | 0.88 | 0.33 |
| Pyridine | 23 | 1.21 | 1.00 | 0.21 | 0.96 | 0.67 | 0.29 |
| Quinoline | 47.3 | 1.63 | 1.48 | 0.15 | — | — | — |
| Aniline | 38 | 1.63 | 1.30 | 0.33 | 1.72 | 0.91 | 0.80 |
| N-Methylaniline | 39 | 1.63 | 1.32 | 0.31 | — | — | — |
| N,N-Dimethylaniline | 35 | 1.50 | 1.24 | 0.26 | 1.10 | 0.86 | 0.14 |
| $\alpha$-Naphthylamine | 64 | 2.18 | 1.81 | 0.37 | 2.62 | 1.32 | 1.30 |
| $\beta$-Naphthylamine | 64 | 2.14 | 1.81 | 0.33 | — | — | — |
| Diphenylamine | 78 | 1.85 | 2.09 | —0.24 | 1.76 | 1.54 | 0.22 |
| Pyrrole | 21.2 | 1.61 | 0.96 | 0.65 | — | — | — |
| Indole | 47.0 | 2.08 | 1.47 | 0.61 | 1.71 | 1.05 | 0.66 |
| Carbazole | 74.0 | 2.47 | 2.01 | 0.46 | 2.03 | 1.48 | 0.55 |

[a] Ref. 6.
[b] Ref. 3.

values were calculated using eqns. 1 and 2. Differences between experimental and calculated values are also listed in Table II.

As can be seen there is considerable difference between calculated and experimental values if the aromatic contains heteroatoms; $\pi$ cloud bonding is then only a part of the adsorption process. An analysis of the results is given below.

The three nonplanar hydrocarbons: biphenyl, *trans*-stilbene, and 9,10-dihydroanthracene all give experimental values less than the computed values. This appears reasonable in view of the fact that the nonplanarity prevents the simultaneous interaction of the $\pi$ cloud with the gels as is possible for the planar compounds. Diphenylamine in methanol and benzophenone in isopropanol also give too low values as might be expected from nonplanar molecules.

Values for all other compounds are too high compared to calculated values implying bonding by other mechanisms as noted by BROOK AND MUNDAY[1]. Since all the compounds tested contain either oxygen or nitrogen atoms, hydrogen bonding from or to the gel appears most likely.

In methanol all aniline derivatives and naphthyl amines give values which on the average are 0.32 ± 0.04 units too high. This can be accounted for by bonding to a hydrogen in the gel since N,N-dimethylaniline shows a $K$ value 0.26 units in excess of the calculated value. Since this is the lowest value for the amine derivatives there is probably a partial contribution from –NH bonding to oxygen in the gel.

The higher disparity for phenol (0.39 units) and the fact that anisole also gives too high a value implies that hydrogens in the gel readily bond to oxygen in these compounds.

The pyrrole derivatives (pyrrole, indole, and carbazole) give values that are 0.57 ± 0.10 units too high (methanol) indicating strong hydrogen bonding from the acidic imide hydrogen to the gel. A similar effect is noted in isopropanol.

Pyridine and quinoline which have no hydrogens on the nitrogen give lower differences from calculated values than either the pyrrole or aniline derivatives. Since hydrogen bonding to these compounds must come from hydrogens on the gel, the counter bonding abilities of the pyrroles are emphasized.

The most puzzling case is benzoic acid. Its $K$ value is very closely approximated

TABLE III

HYDROGEN BOND ENERGIES FOR COMPOUNDS ON SEPHADEX LH-20 IN METHANOL

| Compound | Hydrogen bond energy (kcal) |
|---|---|
| Anisole | 10 |
| Phenol | 20 |
| Aniline | 17 |
| N-Methylaniline | 16 |
| N,N-Dimethylaniline | 13 |
| 1-Naphthylamine | 18 |
| 2-Naphthylamine | 16 |
| Pyridine | 11 |
| Quinoline | 8 |
| Pyrrole | 32 |
| Indole | 30 |
| Carbazole | 23 |

by the calculated value. Hydrogen bonding is to be expected unless steric factors interfere with bonding to the carboxyl group.

Assuming that the only two possible types of bonding for all compounds are $\pi$ and hydrogen bonding and that the $\pi$ bonding energy is equal to the resonance energy, the hydrogen bonding energies can be computed from eqn. 1 and experimental values of $K$. These values are listed in Table III. With the exception of the pyrrole derivatives they are all less than 20 kcal. Only in the case of pyrrole does this energy constitute the majority of the bonding energy for any compound.

## CONCLUSIONS

Adsorption values for planar aromatic hydrocarbons on Sephadex LH-20 correlate very well with resonance energy values implying bonding is through the $\pi$ electron cloud. This is found when either methanol or isopropanol is the solvent.

Nonplanar aromatic hydrocarbons do not show this correlation evidently because the total $\pi$ cloud cannot be utilized as efficiently as in the planar compounds.

Nonplanar aromatic compounds containing oxygen and nitrogen atoms show the same behavior as nonplanar hydrocarbons.

Planar aromatic compounds containing oxygen and nitrogen atoms are more strongly adsorbed on the gel than predictable by the resonance energies.

The experimental evidence indicates that the gel LH-20 exhibits the properties of both a soft and hard acid in PEARSON's terminology[7] since it utilizes both $\pi$ electron acceptor sites and hydrogen bonds to adsorb molecules.

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