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## THE PHYSICO-CHEMICAL FUNDAMENTALS OF GAS CHROMATOGRAPHIC RETENTION ON POROUS POLYMER COLUMNS: PORAPAK Q AND T

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## SUMMARY

In order to explain the retention behavior of organic adsorbates on porous polymer columns in gas chromatography an attempt was made to derive characteristic functional group incremental energies for the nonpolar Porapak Q and very polar Porapak T. The total adsorption energies of a series of characteristic organic compounds were calculated and the corresponding functional group values were derived using the incremental energy equations. It has been demonstrated that Porapak T exhibits a characteristic strong interaction with the oxygen atom in alcohols, ethers and ketones and very likely has the same intensity with the hydroxyl hydrogen. Porapak Q, on the other hand, shows repulsion or weak interaction with a hydroxyl, ether or ketone oxygen but strongly interacts with the hydroxyl hydrogen. The particularly high values of the  $\text{CH}_3$  group incremental energies were calculated and discussed.

## INTRODUCTION

Porous polymers, mostly crosslinked polystyrene copolymers, were originally developed for use in gel permeation chromatography, but their outstanding physical properties have made them a very popular column packing in gas chromatography. The main reason for their wide use as separating media in gas chromatography lies in their excellent performance in handling a great number of compounds which until now could not be analyzed at all or only with difficulty. Although organic in nature, porous polymers have been found to separate most of the inorganic gases very efficiently and, in addition, all classes and types of organic compounds. Out of nearly one hundred and fifty papers published in this field, almost half deal with the elution of pure inorganic, or mixtures of organic and inorganic compounds. A review of the literature data, however, shows very inconsistent information regarding elution from porous polymer columns. This deals with the possibility (or impossibility) of the elution of certain classes of compounds, reversed order of elution, trace analysis, column efficiency, etc. Regardless of these facts, porous polymers are undoubtedly superior

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to any known conventional column packing where the separation and trace analysis of glycols, polyols, amines and mixtures of organic with inorganic compounds is concerned.

Another major controversy concerning porous polymers is their mechanism of retention. In order to draw attention to their particular properties concerned in gas chromatographic separations HOLLIS<sup>1</sup> proposed the name gas gel chromatography for the technique, a term used earlier by LYSYJ AND NEWTON<sup>2</sup> when describing polytrifluoromonochloroethylene column packings. It is a generally accepted idea that the retention mechanism on porous polymers is rather complex and that both adsorption and solution mechanisms are involved at least at higher temperatures. The rather limited experimental evidence presented so far tends to support this idea. At the present stage of research it is rather difficult to distinguish, conveniently, between the two phenomena, solution and adsorption taking place simultaneously. Some insight into the problem is offered, however, by investigation of the column dynamics<sup>3</sup>, determination of the adsorption isotherms<sup>4</sup>, and finally apparent adsorption-desorption times.

In this paper, however, another approach to explain the retention phenomena is discussed, energy changes in the organic adsorbates-porous polymers systems being considered. This way, the real nature of the retention is not ascertained, *i.e.*, whether it is, and to what extent, adsorption or solution, but the problem is investigated from the standpoint of molecular interactions regardless of at what physical state of the column packing these interactions are taking place. For the sake of convenience, however, and since porous polymers are very rigid macroporous beads of determined surface area, we are calling our treatment an investigation of the adsorptive properties of the porous polymers. This may not be quite correct but will certainly be a next best approximation. The treatment involves the gas chromatographic determination of the adsorption enthalpies of a series of characteristic organic compounds and the evaluation of functional group adsorption energy increments. Of sixteen commercially available porous polymers Porapak Q and Porapak T (Waters Associates) were chosen because of their characteristic properties. Porapak Q has a nonspecific, nonpolar surface, while Porapak T seems to be the most polar porous polymer available, capable of long retention of polar compounds, unlike Porapak Q, which shows quite low adsorptivity of polar and particularly oxygenated materials. These two representatives of the porous polymers were therefore chosen by reason of their surface characteristics rather than their wide applicability. Some other brands of porous polymers would show even better separation capabilities in some instances.

#### EXPERIMENTAL

Adsorption enthalpies were derived from the slope of a straight line  $\log k'$  (capacity ratio) against  $1/T_c$ . Retention times were determined from the recorder chart paper and flow rates were measured with soap bubble flowmeter and adjusted to a rate of about 20 ml/min of molecular sieve dried helium (Matheson), which was used as carrier gas. Columns packed with Porapak Q and Porapak T were stainless steel (2 ft. long  $\times$  1/8 in. diameter fitted into a Hewlett-Packard Model 5754A gas chromatograph). The temperature was chosen so as to give reasonable retention

times of about 10 min, or more, and read using precision thermometers to the nearest 0.1°. Three to five groups of retention time measurements within a range of about 20° were carried out, each group containing at least five determinations. The slope of the straight line  $\log k'$  against  $1/T_c$  was derived by means of the least squares method.

Because of the tendency of porous polymers to exhibit tailing, even at low sample sizes, the amount of sample injected was kept as small as possible. Thermal conductivity detection (at the highest sensitivity setting) was applied by reason of convenient and frequent flowrate measurement. Sample sizes were actually of a "zero volume" representing the volume of liquid which penetrated by capillary action into the 1  $\mu$ l Hamilton syringe when the very tip of the needle (with plunger positioned at zero) was dipped for one second into a liquid sample. The recorded peaks were broad but symmetrical, being very convenient for the retention measurements. The samples were commercial high purity chemicals used without further purification; *viz.* homologous series of C<sub>1</sub>-C<sub>4</sub> *n*-alcohols, C<sub>2</sub>-C<sub>5</sub> *n*-alkanes, isopropanol, *tert.*-butanol, acetone, diethyl ether, benzene, cyclohexane and water. Throughout the rest of the text all adsorption energies are expressed in - kcal/mole unless otherwise specified.

## RESULTS AND DISCUSSION

In contrast to gas-liquid chromatography, the gas-solid chromatographic determination and treatment of the thermodynamic parameters seem to be more convenient. In practice, however, one usually meets one or several disadvantages with gas-solid chromatography, *e.g.*, nonlinearity (or a narrow range of linearity) of adsorption isotherms originating in the hydrodynamic and/or thermodynamic properties of the adsorbent surface, and pore size distribution. Furthermore, in order to derive meaningful adsorption thermodynamic data extremely small surface area coverages are of critical importance, in order to avoid excess lateral (adsorbate-adsorbate) interaction. Usually, the surface coverage should be kept below 0.1, though even at this low coverage unfavorable pore size distribution can produce unreasonably high results of the order of several kcal/mole of adsorption energy due to excess radial dispersion interactions within the narrow pores.

The adsorption energy of a molecule generally appears to be a much more important thermodynamic parameter than the entropy or free energy of adsorption, since theoretically and experimentally the entropy values are a less sensitive measure of molecular interactions<sup>5</sup>. On the other hand, like molecular polarizability or dipole moments, the heat of adsorption of a molecule is actually an integral of the "local" or incremental adsorption energy of each characteristic functional group. This applies regardless of the origin of the adsorption energy, whether it is a product of pure dispersion (nonspecific) interaction or electrostatic or induction interaction, and is usually denoted as a specific part of the adsorption energy<sup>6</sup>. Total adsorption energy is moreover the sum of dispersion (nonspecific), polarization and dipole interaction, and since the constants of molecular interactions are proportional to polarizability, the difference between total and nonspecific interaction would reveal the amount of specific interaction. It is necessary to point out that in nonspecific adsorption interaction the retention parameters definitely do not depend upon boiling points (being just a measure of adsorbate-adsorbate interaction), dipole moments, molecular size and weight but depend on molecular polarizability and indirectly on the stereochem-

istry of the adsorbate molecule. In specific interactions, involving adsorbents with the electrostatic field on the surface, the adsorbate's electron distribution (dipole moments) is overwhelmingly important.

In the explanation of retention behavior, or in fact molecular adsorbate-adsorbent interactions, particularly when the adsorbate appears to be a more or less complex organic molecule, it is very interesting to derive characteristic functional group adsorption energy increments, specific and nonspecific as well. Actually, the concept of incremental energy quantities in gas chromatography has been found very effective in explaining particular molecular interactions in both GLC<sup>7,8</sup> and GSC<sup>9,10</sup>.

TABLE I

HEATS OF ADSORPTION, SPECIFIC INTERACTIONS EXCESS ADSORPTION HEATS AND POLARIZABILITY OF ORGANIC ADSORBATES ON PORAPAK Q AND T

Compound	$-\Delta H_a$ (kcal)		$\Delta(\Delta H_a)$ T - Q (kcal)	$\Delta H_v$ (kcal)	$\Delta H_a - \Delta H_v$		Polarizability, $\alpha$ , $\times 10^{24}$ cm <sup>3</sup>
	Porapak Q	Porapak T			Porapak Q	Porapak T	
Water	7.7	9.5	1.8	9.7	+2.0	+0.2	1.5
Methanol	8.7	10.8	2.1	8.5	0.2	2.3	3.9
Ethanol	10.3	12.4	2.1	9.3	1.0	3.1	5.6
<i>n</i> -Propanol	11.9	13.9	2.0	10.0	1.0	3.9	7.3
Isopropanol	10.2	13.2	3.0	9.7	0.5	3.5	8.4
<i>n</i> -Butanol	14.0	15.8	1.8	10.5	3.5	5.3	9.5
<i>tert.</i> -Butanol	11.5	12.9	1.4	9.6	1.9	3.3	—
Acetone	9.7	12.7	3.0	7.0	2.7	5.7	6.6
Diethyl ether	8.2	12.0	3.8	6.4	1.8	5.6	10.0
Cyclohexane	13.0	13.6	0.6	7.2	5.8	6.4	11.0
Benzene	12.9	14.2	1.3	7.4	5.5	6.8	10.4
Propane	8.7	7.7	+1.0	4.5	4.2	3.2	6.3
Butane	10.0	9.0	+1.0	5.3	4.7	3.7	8.2
<i>n</i> -Pentane	11.3	10.3	+1.0	6.2	5.1	4.1	10.0

The results of measurements of heats of adsorption on Porapak Q and T are presented in Table I. Since Porapak Q (a styrene-ethylvinylbenzene-divinylbenzene co-polymer) is nonpolar and therefore a *nonspecific* adsorbent, heats of adsorption derived for this adsorbent are considered as the quantities for a nonspecific interaction, in contrast to the generally higher values of the adsorption energy obtained for the polar Porapak T. As a result of the presence of benzene rings in the Porapak Q structure there is some possibility of weak specific interactions with the adsorbate molecules having local positive charges, *e.g.* alcohols. The structure of the really more interesting Porapak T has not yet been disclosed by the manufacturers, thus corresponding thermodynamic quantities have no real chemical interpretation. SAKODYNSKY<sup>11</sup> indicated the presence of a positive charge on the surface of Porapak T, thus giving an excess specific interaction energy term and making this porous polymer particularly suitable for the retention of oxygenated materials and compounds having free electron pairs (*e.g.* ethers and ketones) but rather insensitive towards compounds having  $\pi$ -bonds. Reading the difference, or the specific interaction energy from the third column in Table I, these conclusions are confirmed, further indicating the relatively low adsorption energy of isopropanol on Porapak Q, which is readily explain-

able in view of the stereochemistry of this compound. On the other hand, the value of the adsorption energy of isopropanol on Porapak T indicates that this interaction has suffered a much lower loss, if any at all. Thus the high specific interaction energy of isopropanol is more conveniently explained by the apparent loss in the nonspecific dispersion interaction, due to a diminution in the total number of electron orbitals involved in the adsorbate-adsorbent interaction. On the other hand, the higher specific energy of benzene compared to cyclohexane is due to the more polarizable  $\pi$ -electrons of the benzene ring.

The particularly notable decrease in the adsorption energy of *n*-alkanes on Porapak T is less explainable in view of the unknown chemical structure of this adsorbent, but this phenomenon otherwise completely corresponds to the adsorption behavior of alkanes on other adsorbents. For example the heat of adsorption of alkanes on silica gels (a specific adsorbent of the same general type as Porapak T — *electron acceptors*) is also lower than on a nonspecific adsorbent like graphitized carbon black<sup>10</sup>. Although it is an inorganic compound, water is included in this table because of the particular interest and low retention of water on Porapak Q columns. The value of 1.8 kcal for the specific interaction of water is about one third of an expected value for hydrogen bonding in liquid water. However, the Porapak Q-water system is another environment completely so that the total figure for the specific interaction fits well in the range of hydrogen bond energies. The large difference in the heats of absorption found for diethyl ether and acetone is plausible in view of the above discussion.

Although not of direct use here, the heats of vaporization of adsorbates are also tabulated and the excess heat of adsorption calculated. As mentioned earlier in this paper, the heat of vaporization has no connection with the adsorption phenomenon at low coverages but can be used just for comparison purposes here, although excess adsorption functions have been discussed in some detail recently<sup>12</sup>. The molecular polarizability values for each adsorbate are presented in Table I (last column); these are very important in further discussions on the adsorption phenomena. On the other hand very sparse and incomplete data exist in literature concerning thermodynamic measurements on porous polymers-organic adsorbate systems. GVOZDOVICH *et al.*<sup>13</sup> mentioned a heat of adsorption of H<sub>2</sub>O on a home made styrene-divinylbenzene copolymer of about 6 kcal; this is lower than that for all lower molecular weight organic compounds. SAKODYNSKY<sup>11</sup> plotted the heats of adsorption for a series of alcohols and alkanes against polarizability but with no particular mention of what porous polymers were concerned and without tabulating pertinent data.

The usual plot of the adsorption energy against polarizability for the adsorbates mentioned is presented in Fig. 1, where data for both Porapaks and the difference T — Q is plotted. Converging straight lines for *n*-alcohols are obvious because of the slow diminution of specific interactions for higher members of the homologous series. In Fig. 2 a similar plot is presented for two homologous series of *n*-alcohols and *n*-alkanes, showing the particular properties and behavior of these compounds on both Porapaks.

A more realistic view on the nature of the molecular interactions in the process of adsorption is obtained by studying functional group adsorption energy increments. This concept is based upon the already discussed additivity of the potential energy terms of dispersion and electrostatic interaction<sup>10</sup>. Some of the equations for expressing

incremental energy quantities listed in ref. 10 were modified to suit the purpose of this work; rearranged equations are presented in Table II. Using the data on total adsorption energy presented in Table I, the values of the functional group energy increments can be derived, and are presented in Table III. For comparison purposes, the results obtained for a nonspecific adsorbent, graphitized carbon black (GCB)<sup>10</sup>, are also included in Table III.

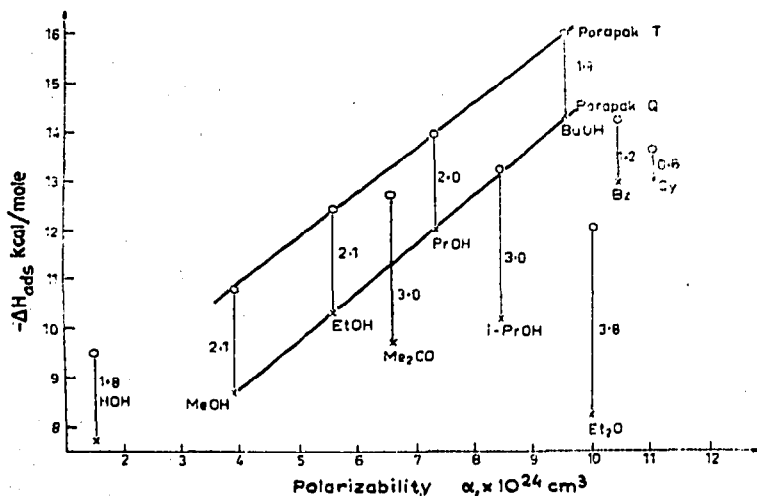


Fig. 1. The plot of the heats of adsorption against polarizability for various adsorbates on Porapak Q (×) and Porapak T (○).

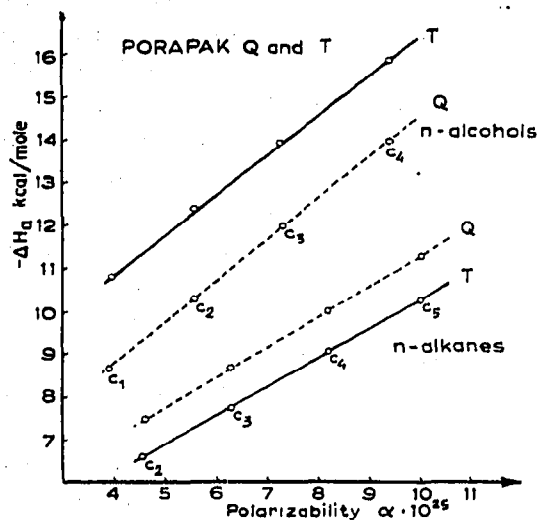


Fig. 2. The plot of the heats of adsorption against polarizability for a homologous series of *n*-alcohols and *n*-alkanes on Porapak Q (---) and Porapak T (—)

As can be observed no mention of other characteristic functional groups, such as  $\text{NH}_2$ ,  $\text{COOH}$  and  $\text{CHO}$ , has been made, since the elution of corresponding compounds from the porous polymers tested has stirred up considerable controversy. If the values in Table III are studied one can immediately notice a slight increase in the value for the  $\text{CH}_2$ -alcohol increment over that of the alkane methylenic group for both Porapaks, a fact which has not been recorded for other adsorbents. Furthermore,

a quite unexpected result is obtained for the methyl group increment showing a 2.4 and 1.9 kcal/mole increase over the value for the CH<sub>2</sub> increment for alkanes on Porapak Q and T, respectively. At present, there are insufficient data on the subject for a reasonable explanation; furthermore, it is worth mentioning that the CH<sub>3</sub> increment, even

TABLE II  
ADSORPTION ENERGY INCREMENT EQUATIONS

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$$\Delta H_{\text{CH}_2} \text{— alkanes } C_n, \text{ alcohols}$$

$$\Delta H_{C_n} - \Delta H_{C_{n-1}}$$

$$\Delta H_{\text{CH}_3} \text{— alkanes}$$

$$1/2[\Delta H_{C_n} - (n-2)\Delta H_{\text{CH}_2}]$$

$$\Delta H_{\text{O}} \text{— ether}$$

$$\Delta H_{C_n\text{OC}_m} - \Delta H_{C_nC_m}$$

$$\Delta H_{\text{O}} \text{— ketone}$$

$$\Delta H_{(C_nC_m)\text{CO}} - \Delta H_{C_n\text{CH}_2C_m}$$

$$\Delta H_{\text{OH}} \text{— alcohol}$$

$$\Delta H_{C_n\text{OH}} - \Delta H_{C_n}$$

$$\Delta H_{\text{H}} \text{— hydroxyl (water, alcohols)}$$

$$1/2(\Delta H_{\text{H}_2\text{O}} - \Delta H_{\text{O-ether}})$$


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on highly polar adsorbents (molecular sieves), usually has a value no higher than 0.3 kcal over that for the CH<sub>2</sub> value. Another interesting phenomenon is the slight endothermic specific (repulsion) interaction of the CH<sub>3</sub> group on polar Porapak T in comparison with Porapak Q. It is obvious from the foregoing that the CH<sub>3</sub> group behaves in a manner which is peculiar and not conveniently explainable in terms of an ordinary adsorption mechanism. We believe that here lies the origin of the specific properties of porous polymers demonstrated in the gas chromatographic retention of organic molecules, exhibiting presumed adsorption–solution effects. It is, however, interesting to mention here that the heat of vaporization energy increments for alkanes demonstrate similar trends, a CH<sub>2</sub> increment equals 0.8–0.9 kcal while the CH<sub>3</sub> amounts to about 1.9 kcal.

While the values of the incremental energies of the hydroxyl group of alcohols show the expected trend the value of a protonic hydrogen in OH groups is definitely very interesting, because of the rather high values on Porapak Q indicating that certain specific interaction mechanisms must have taken place. In other words, that the surface of Porapak Q is slightly negative or polarizable; this can be concluded from the foregoing discussion. A value of 3.3 kcal for the incremental energy of a

TABLE III  
FUNCTIONAL GROUP ADSORPTION ENERGY INCREMENTS IN —KCAL/MOLE

Functional group	Q	T	T - Q	GCB <sup>10</sup>
CH <sub>2</sub> -alcohol	1.6	1.6	0	1.6
CH <sub>2</sub> -alkanes	1.3	1.3	0	1.6
CH <sub>3</sub> -alkanes	3.7	3.2	+0.5	2.1
OH-alcohols	3.2-4	6.2-6.8	2.8-3.0	2.1
H-alcohols OH, H <sub>2</sub> O	4.7	3.3	+1.4	0.7
O-ethers	+1.8	3.0	4.8	1.3
O-ketones	1.0	5.0	4.0	—

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protonic hydrogen on Porapak T, in view of the positive electrostatic potential on its surface, is unexpectedly high, leaving approximately the same interaction energy for the oxygen atom of the hydroxyl group, a quantity which can be further identified as the increment of an ether oxygen. The endothermic incremental energy of the ether oxygen on Porapak Q seems to favor the assumption that there is a strong repulsion of either free electron pairs or negatively charged atoms or groups. These findings are partially in agreement with the adsorption energy values reported by SAKODYNSKY<sup>11</sup> who found a value of  $-10.8$  kcal for *n*-pentane and  $10.4$  kcal for diethyl ether on an unspecific porous polymer, presumably a styrene-divinylbenzene copolymer. In our case, the adsorption energy of diethyl ether on Porapak Q is even lower than that of propane (Table I).

The value for the incremental energy of a carbonyl oxygen (acetone) is higher by  $2.8$  kcal than that for the ether oxygen on Porapak Q and is obviously due to a completely different electronic environment and the possibility, under favorable conditions, of an eventual enolic interaction in this way obscures the true oxygen interaction potential. In any case, it is obvious that the high specific interaction of the oxygen atom in organic molecules (difference T — Q) is responsible for the favorable retention of these compounds on Porapak T. On the other hand, Porapak T seems to interact to some extent with the OH hydrogen, although to a smaller degree than Porapak Q. This result, as well as the strong repulsion of the ether oxygen indicates that Porapak Q is not a completely nonspecific adsorbent.

The above treatment illustrates the very interesting properties of porous polymers as column packings in gas chromatography. It can be demonstrated that both Porapak Q and T show characteristic interactions with specific functional groups, carrying an electric charge or free electron pairs. These preliminary results show great promise for further work on these interesting systems. The retention indices determined for a great number of compounds<sup>14,15</sup> show that very interesting molecular interactions are certainly taking place during the elution of a number of different compounds. In this laboratory an extensive investigation is under way covering a number of characteristic simple inorganic and organic compounds and the results will be published later.

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