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COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

II. INTERACTIONS OF HYDROCARBONS WITH POLY[CHROMIUM(III) DIPHENYLPHOSPHINATE]: CALCULATION OF STABILITY CONSTANTS OF π-COMPLEXES IN GAS–SOLID CHROMATOGRAPHY

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SUMMARY

The interactions of hydrocarbons with poly[chromium(III) diphenylphosphinate] have been studied. Comparison of the interactions of hydrocarbons with adsorbents conditioned at 250 and 330° C indicates the possibility of formation of chromium–unsaturated hydrocarbon π-complexes for the adsorbent conditioned at the higher temperature. A method of calculation of stability constants of surface π-complexes from gas–solid chromatographic data is given.

INTRODUCTION

A quantitative relation between the structure of compounds and their interaction with adsorbent surfaces has not yet been described in the literature. The qualitative scheme of Kiselev and Yashin[1] divides adsorbate–adsorbent interactions into specific and non-specific classes. According to these workers, dispersion forces are responsible for non-specific interactions. King and Benson[2,3] have assumed that the nature of non-specific interactions has an electrostatic origin. Gerber and Sawyer[4] have found that non-specific interactions can be related to a non-localized adsorption.

The previous paper of this series[5] described the application of a coordination polymer of chromium(III) with diphenylphosphinic acid (DPP–Cr) as the adsorbent in gas chromatography. This polymer displayed specific interactions with unsaturated hydrocarbons (demonstrating the existence of π-complexes on the adsorbent surface) only after being conditioned at 330° C. No such properties were exhibited by DPP–Cr conditioned at temperatures below 250° C. In this paper we attempt to compare interactions between hydrocarbons and adsorbents containing DPP–Cr conditioned at 250 and 330° C with theoretical values calculated on the assumption of non-localized adsorption. We also check the applicability of the theory of King and Benson to the evaluation of these adsorbents, and quantitatively estimate the interactions resulting from the formation of surface π-complexes.

EXPERIMENTAL

The apparatus and procedure were as described previously[5]. The complexing packing 3% DPP–Cr–Spherosil XOB-030–dimethyldichlorosilane (DMCS), was conditioned at 330° C. The reference packings, 3% DPP–Cr–Spherosil XOB-030–DMCS and 2% DPP–Cr–silica gel–NH$_4$F–DMCS, were conditioned at 250° C. The packings were placed in stainless-steel columns (1 m × 4 mm). Suitable alkanes were used as reference compounds for the alkenes, and cyclohexane was used as a reference for aromatic hydrocarbons.

The preparation of adsorbents containing 3% DPP–Cr–Spherosil XOB-030–DMCS has been described previously[5]. The adsorbent containing 2% of DPP–Cr–silica gel–NH$_4$F–DMCS was prepared as follows. Silica gel (Koch-Light, Colnbrook, Great Britain) with a specific area of 897 m^2/g was washed with distilled HCl in order to remove Fe^{3+} and other metal ions. Then it was washed with distilled water until a neutral eluate was obtained. Deactivation of the silica gel was carried out according to the procedure described by Elmer et al.[6], which consists in washing with a 30% solution of NH$_4$F for 0.5 h and then with distilled water until a neutral eluate is obtained. The silica gel was dried in an oven at 110° C and then calcined in a furnace at 850° C for 5 h. The gel was then deactivated with DMCS, as carried out previously for Spherosil[5]. In this way deactivated silica gel–NH$_4$F–DMCS with a specific area of 140 m^2/g was obtained. After deposition of 2% DPP–Cr on this carrier, an adsorbent having a specific area of 144 m^2/g was produced.

RESULTS AND DISCUSSION

The type of adsorption can be determined by comparison of theoretical values of the non-localized entropy with experimental values of the adsorption entropy for the standard state. According to Gerber and Sawyer[4], the non-specific interactions in gas–solid chromatography (GSC) belong to non-localized adsorption. The standard entropy of mobile adsorption can be calculated from the equation derived by De Boer and Kruyer[7]:

$$\Delta S_m^\circ = \tfrac{1}{2}R\ln(m^{3/2}T^{5/2}) - 1.522\log T + 2.28$$

where m is the molecular weight of the adsorbate, T is the temperature in °K and R is the gas constant.

Values of the thermodynamic functions of adsorption can be calculated from chromatographic data:

$$\log V_s^T = -\frac{\Delta G'_{ads}}{2.3\,RT} = \frac{\Delta H'_{ads}}{2.3\,RT} + \frac{\Delta S'_{ads}}{2.3\,R}$$

V_S^T is the adjusted retention volume in cm^3/m^2 of adsorbent, $\Delta G'_{ads}$ is the free energy of adsorption, $\Delta H'_{ads}$ is the heat of adsorption and $\Delta S'_{ads}$ is the entropy of adsorption. Assuming that adsorbed molecules are equivalent to a two-dimensional ideal gas, one can solve this equation and obtain the thermodynamic functions of adsorption

in the standard state. Thus, the entropy in the standard state can be calculated from the dependence:

$$-\Delta S^{\circ}_{ads} = -\Delta S'_{ads} - 11.33$$

The adsorbent containing 2% DPP–Cr–silica gel–NH$_4$F–DMCS, conditioned at 250° C, does not show any affinity for alkenes ,when compared with the carrier properties. The coverage of such a large carrier surface area (140 m^2/g) with only 2% of DPP–Cr polymer is sufficient for complete deactivation of the surface, and enables one to eliminate the possibility that the absence of specific interactions results from "compressing" of polymer molecules on to the smaller surface area of Spherosil.

In Table I, theoretical (ΔS_m) and experimental (ΔS_{ads}) entropy values are compared for adsorbents containing DPP–Cr conditioned at 250° C and 330° C. From these results, DPP–Cr conditioned at 250° C can be regarded as a non-specific adsorbent, because the experimental values of the adsorption entropies of aliphatic hydrocarbons are close to the ones calculated for mobile adsorption. The changes in the standard adsorption entropy for DPP–Cr conditioned at 330° C are much higher than the calculated ΔS_m values. This suggests that specific interactions play a part in adsorption on an adsorbent conditioned at 330° C.

TABLE I

VALUES OF MOBILE AND STANDARD ADSORPTION ENTROPIES

A = 2% DPP–Cr–silica gel–NH$_4$F–DMCS conditioned at 250°; B = 3% DPP–Cr–Spherosil XOB-030–DMCS conditioned at 330° C.

Adsorbate	$-\Delta S_m$ (cal·mole^{-1}·°K^{-1})	$-\Delta S^{\circ}_{ads}$ (cal·mole^{-1}·°K^{-1})	
		A	B
Hexane	12.83	16.7	22.0
1-Hexene	12.80	18.3	24.1
trans-3-Hexene	12.80	18.1	23.9
Cyclopentane	12.62	15.0	19.0
Cyclopentene	12.59	15.1	19.8
Cyclohexane	12.80	17.4	20.8
Cyclohexene	12.79	18.0	22.8
Benzene	12.73	16.6	22.9
Toluene	12.89	17.0	26.4
Ethylbenzene	13.03	19.9	29.0
Styrene	13.02	20.1	28.9
Heptane	12.98	19.7	24.7
Octane	13.11	20.1	26.3

The assumption that non-specific interactions are caused by non-localized adsorption is very close to reality in the case of molecules of gases[4]. However, in the case of heavier molecules (e.g., n-alkanes and cycloalkanes) one can say that localized adsorption also contributes to the non-specific interaction. According to Kiselev and Yashin[1], alkanes can interact with adsorbent surfaces only non-specifically. Therefore, these hydrocarbons can be used as reference points for the estimation of specific interactions. The theory of King and Benson[2,3] proposes that these should be a linear dependence of the logarithm of the adjusted retention volume (or time) on the

polarizability of the molecules. This is fulfilled for *n*-alkanes. Moreover, if some deviations of organic molecule from this dependence occur, they can be attributed to specific interactions, and the extent of deviation at a given polarizability value can be regarded as a measure of the strength of the specific interaction. This deviation is proportional to the difference between the free energies of adsorption of a given compound and the *n*-alkane having the same polarizability.

Figs. 1 and 2 show the dependences of the logarithms of the adjusted retention volumes on the molar refraction. (The latter is related to polarizability by a simple dependence and appropriate data are more readily found in the literature.) Fig. 1 concerns the adsorbent containing 3% DPP–Cr–Spherosil XOB-030–DMCS conditioned at 250° C. The points for the alkenes are grouped near the straight line determined by the *n*-alkanes. This shows that there is a weak interaction between olefins and this packing. The straight line determined by the aromatic hydrocarbon series is about 0.4 of a logarithmic unit away from the *n*-alkane line.
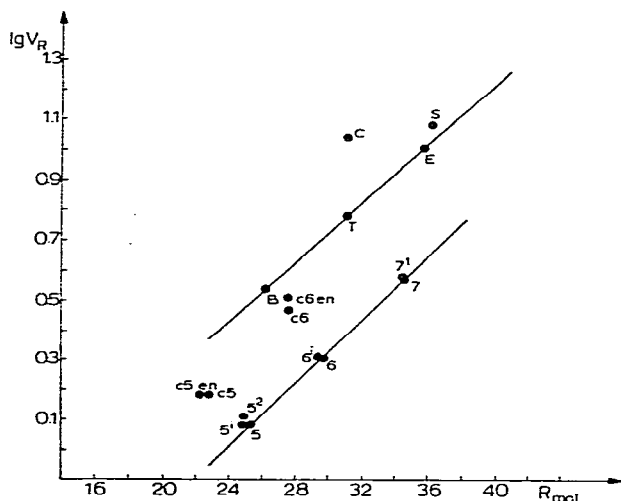

Fig. 1. Logarithms of adjusted retention volumes for a series of hydrocarbons *vs.* their molar refractions using a 3% DPP–Cr–Spherosil XOB-030–DMCS column conditioned at 250° C ($T_k =$ 200 °C). 5 = Pentane; 5^1 = 1-pentene; 5^2 = 2-pentene; c5 = cyclopentane; c5en = cyclopentene; 6 = hexane; 6^1 = 1-hexene; 7 = heptane; 7^1 = 1-heptene; c6 = cyclohexane; c6en = cyclohexene; B = benzene; C = chlorobenzene; E = ethylbenzene; S = styrene; T = toluene.

In Fig. 2 the same dependences are presented for the same packing conditioned at 330° C. The alkene points clearly deviate from the straight line determined by *n*-alkanes. This shows that there are somewhat stronger interactions of the alkenes with the packing conditioned at 330° C than with the same packing conditioned at 250° C. The difference between the logarithms of the retention volumes of benzene and cyclohexane is about three times larger than that between the logarithms of the retention volumes of cyclohexene and cyclohexane. This indicates a participation of the π-electrons of these hydrocarbons in the adsorption process. In the case of the polymer conditioned at 330° C, the difference between the straight lines for aromatic hydrocarbons and alkanes amounts to 0.6 of a logarithmic unit, more than that for DPP–Cr conditioned at 250° C.
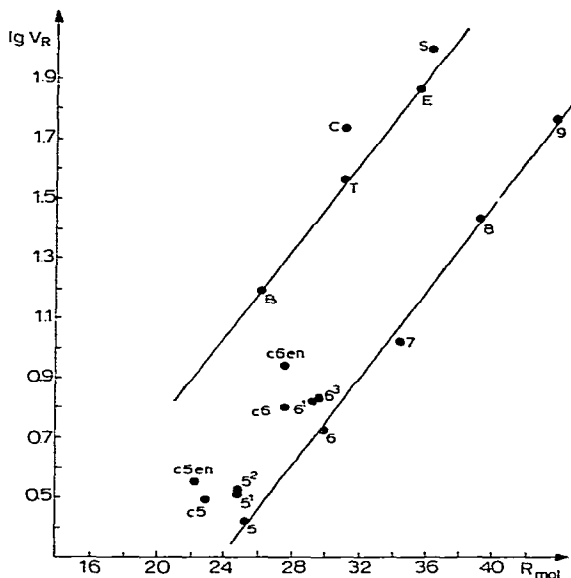
Fig. 2. Logarithms of adjusted retention volumes for a series of hydrocarbons vs. their molar re-
fractions using a 3% DPP–Cr–Spherosil XOB 030–DMCS column conditioned at 330° C (T_k =
200 °C). 6^3 = trans-3-Hexene; 8 = octane; 9 = nonane. Other hydrocarbons as in Fig. 1.

        The observations described above and those discussed in our previous paper[5]
lead to the conclusion that interactions of π-electrons of unsaturated hydrocarbons
with chromium metal are possible. A quantitative estimation of the specific inter-
actions resulting from the formation of surface π-complexes can be made by cal-
culating the stability constants of these adducts. The problem of determining the
stability constants of surface π-complexes from GSC data has not yet been solved.
In only one paper[8] an attempt has been made to calculate the stability constants
of such complexes formed during interactions between La^{3+} and olefins and aromatic
compounds. The model employed was that proposed by Gil-Av and Herling[9] for
calculations of stability constants and which is widely applied in gas–liquid chro-
matography (GLC).
        As we pointed out previously[5], the calculation of the stability constants of
surface π-complexes based on GSC is a difficult matter because of problems connected
with the choice of a suitable reference adsorbent. Such an adsorbent should contain
a reference metal which does not form π-complexes, i.e., a metal of one of the even
series of the periodic system. This metal should also meet the following requirements:
it should have the same charge as a transition metal which forms complexes; its
ionic radius should be very close to that of the investigated transition metal; it
should form a similar compound to the transition metal; the surface concentration
of the reference and complexing metals should be the same; both metals should be
coated on the same carrier.
        In GLC measurements of the stability constants of π-complexes, the metals
of even series are frequently used as references[10]. However, under the conditions
of GSC, these can interact specifically, as was observed by Kiselev and Yashin[1]
who divided adsorbents into specific and non-specific classes. The magnitude of the

specific interactions depends on the charge of cation and its ionic radius[11–13]. The first three limitations concerning a reference metal result from this fact.

It was previously shown[10,14] that the application of relative retention data considerably facilitates experiment and calculations. Therefore, we propose to calculate the stability constants of surface comœlexes by comparison of the relative retention volumes of a compound able to form a complex (*e.g.*, an olefin) and a reference compound which does not form a complex (*e.g.*, a related alkane) on the complexing adsorbent (B') and on the reference adsorbent (S'). Therefore, the stability constant (*K*) of a surface complex can be calculated in a similar way as in GLC, from the formula:

$$\left[\frac{V_A}{V_A'}\right]_{B'} \cdot \left[\frac{V_A'}{V_A}\right]_{S'} - 1 = K \cdot c_B$$

where B' is the adsorbent containing a metal of concentration c_B mole/m² forming a surface complex, S' is the adsorbent containing a reference metal of concentration c_B, V_A is the retention volume of a compound capable of forming a complex and V_A' is the retention volume of a reference compound that does not form a complex.

The results presented in the our previous paper[5] suggest that the formation of π-complexes between olefins, aromatic compounds and chromium in poly[chromium(III) diphenylphosphinate] is possible. Since DPP–Cr exhibits specific interaction with olefins and aromatic compounds only after conditioning at 330° C, we have taken as a reference phase the same packing conditioned at 250° C. Such a reference does not interact specifically with unsaturated hydrocarbons. Thus, all the requirements necessary for calculating the stability constants of surface π-comlpexes are fulfilled. The surface concentration of Cr^{3+} was $6.81 \cdot 10^{-6}$ mole/m². The stability constants were calculated on the assumption that all chromium atoms are able to form π-complexes. The results of the calculations are presented in Table II.

The heats of formation of the complexes were calculated from the temperature dependence of the stability constants. Their values are also given in Table II. Aromatic hydrocarbons form stronger π-complexes than olefins. This is caused by

TABLE II

STABILITY CONSTANTS (*K*) OF SURFACE π-COMPLEXES AND THEIR HEATS OF FORMATION (ΔH_f)

Adsorbate	K $(10^4 \cdot m^2/mole)$			$-\Delta H_f$ $(kcal/mole)$
	150.8°	200.2°	249°	
1-Pentene	5.72	3.67		3.58
cis-2-Pentene	4.27	2.99		2.87
Cyclopentene	3.91	2.64		3.17
1-Hexene	4.84	3.23		3.26
Cyclohexene	6.13	3.74		3.98
Benzene	31.30	9.37	3.71	9.54
Toluene		17.05	8.09	7.46
Ethylbenzene		20.31	11.68	5.54
Styrene		26.34	14.93	5.68
Chlorobenzene		10.42	8.44	2.11

the higher electron density in the aromatic compounds. The inductive effect of a chloride atom on the electrons of the nucleus is manifested by a decrease in the stability constant of the π-complex of chlorobenzene in comparison with that of ethylbenzene, and by the negligible heat of complex formation. These data demonstrate the contribution of the ring electrons to the adsorption process and this is a confirmation of conclusions drawn previously.

It is interesting to compare the stability constants of surface π-complexes of some hydrocarbons formed with lanthanum[8] and chromium (Table III). The numerical values cannot be directly compared because of the different methods of calculation and different reference adsorbents. However, in both cases the same trends can be seen. Thus, 1-hexene has the lowest K value, the stability constants of complexes with aromatic hydrocarbons increases in the order benzene < toluene < ethylbenzene, and the electron-withdrawing effect of Cl on the K value is evident by comparison of the values for chlorobenzene and ethylbenzene.

TABLE III

COMPARISON OF STABILITY CONSTANTS OF SURFACE π-COMPLEXES AT 200°

Compound	K $(m^2/mole)$	
	$LaCl_3$ (ref. 8)	DPP–Cr
1-Hexene	$1.62 \cdot 10^5$	$3.23 \cdot 10^4$
Benzene	$2.09 \cdot 10^5$	$9.37 \cdot 10^4$
Toluene	$4.37 \cdot 10^5$	$17.05 \cdot 10^4$
Ethylbenzene	$5.06 \cdot 10^5$	$20.31 \cdot 10^4$
Chlorobenzene	$2.17 \cdot 10^5$	$10.42 \cdot 10^4$

Hence, one can conclude that the stability of the π-complexes aetermines the sequence of elution of the discussed compounds. The method of calculation of the stability constants of surface π-complexes presented above has all the advantages of methods based on relative retention volumes[10]. However, there are difficulties connected with the requirement of equal surface concentrations of the reference and complexing metals.

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