The Heats of Adsorption on a Silica-gel of some Polar and Apolar Organic Vapours

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The heats of adsorption of CCl_4, $CHCl_3$, CH_2Cl_2, CH_3-CCl_3 and $CH_2Cl-CHCl_2$ on γ-alumina, determined by the gas chromatographic procedure and reported in a previous paper[1], allowed to evidence, for polar molecules, an electrostatic interaction contribution to the adsorption energy and to obtain information about the orientation of adsorbed molecules. Determinations extended to the adsorption of the same and of a few other vapours (CH_2Cl-CH_2Cl, cyclohexane, cyclohexene and benzene) on silica-gel are reported in the present note.

All chemicals were purified according to standard methods.

The adsorbent was C. Erba silica-gel "for gas chromatography": a fraction was chosen with grain size 80–120 mesh (ASTM) and BET nitrogen surface area $655 \pm 9\ m^2/g$. The sample was activated before column packing by heating in air at 220 °C for some hours and then by flushing the packed columns with the carrier gas for additional 6–8 hours at 200–220 °C.

The experimental set-up and procedure, as well as the evaluation of the adsorption heat from the gas chromatographic retention times were substantially the same as already described[1]. It can be noted that, owing to the fact that the surface area of the silica-gel is much larger than that of the γ-Al_2O_3 employed previously ($\approx 150\ m^2/g$), significantly higher values of the pressure gradient across the column and of the carrier-gas flow-rate had to be adopted to obtain reasonable values of the retention times over the whole temperature range. Duplicate independent runs were made for most adsorbates in order to check the reproducibility, the experimental conditions being summarized in Table 1.

Table 1. Gas-chromatographic conditions.

Column: stainless steel, length 100 cm, i. d. 0.6 cm
Carrier gas: hydrogen (electrolytic, 99.995%)

Adsorbate	Run	Temperature range [°C]	Flow rate [ml/min]	Pressure drop range [atm]
Cyclohexane	1	175–220	100	0.94–0.99
	2	170–210	120	1.00–1.08
Cyclohexene	1	195–230	180	1.35–1.46
	2	195–230	180	1.35–1.44
Benzene	1	198–230	150	1.22–1.29
	2	195–230	200	1.48–1.58
CCl_4	1	180–220	150	1.13–1.23
	2	185–225	150	1.13–1.24
$CHCl_3$	1	180–220	150	1.12–1.23
	2	180–220	150	1.12–1.22
CH_2Cl_2	1	180–220	100	0.82–0.90
	2	185–225	100	0.83–0.91
	3	185–225	100	0.83–0.92
CH_3-CCl_3	1	188–230	80	0.69–0.77
	2	188–230	80	0.69–0.77
$CH_2Cl-CHCl_2$	1	205–230	200	1.45–1.52
CH_2Cl-CH_2Cl	1	195–230	200	1.41–1.52
	2	195–230	200	1.41–1.52

Cyclohexane	μmol	0.90	2.80	4.55	6.50	9.20	18.50
	Q_a	9.33	9.29	9.29	9.27	9.23	9.21
Cyclohexene	μmol	1.97	3.95	5.92	7.89	9.86	19.73
	Q_a	10.95	10.92	10.88	10.88	10.86	10.85
Benzene	μmol	2.25	4.50	6.75	9.00	11.25	22.51
	Q_a	11.37	11.29	11.28	11.27	11.27	11.28
CCl_4	μmol	2.06	4.12	6.18	8.24	10.30	20.59
	Q_a	9.41	9.40	9.36	9.32	9.33	9.28
$CHCl_3$	μmol	2.48	4.96	7.44	9.92	12.40	24.79
	Q_a	9.68	9.64	9.64	9.63	9.65	9.61
CH_2Cl_2	μmol	3.21	6.41	9.62	12.83	16.04	32.07
	Q_a	9.27	9.24	9.25	9.24	9.28	9.35
CH_3-CCl_3	μmol	1.98	3.96	5.95	7.92	9.90	19.80
	Q_a	8.87	8.91	8.94	8.97	9.00	9.11
$CH_2Cl-CHCl_2$	μmol	4.32	7.56	10.79	21.59		
	Q_a	12.86	12.80	12.76	12.70		
CH_2Cl-CH_2Cl	μmol	2.53	5.06	7.60	10.13	12.66	25.32
	Q_a	11.35	11.37	11.35	11.33	11.32	11.31

Table 2.
Heats of adsorption, Q_a (kcal/mol), measured for different injected sample amounts (μmol).

The standard deviation of Q_a[2] was comprised in the range 0.3–0.4 kcal/mol for the cyclic hydrocarbons and for 1.1.2-trichloroethane, and in the range 0.1–0.2 kcal/mol, or even less, for all other adsorbates.

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The heats of adsorption, Q_a, evaluated from the straight-line plots $\log t$ *vs.* $1/T$ for each injected amount, are reported in Table 2, limitedly to one representative run for each adsorbate. On plotting these Q_a values *vs.* the injected amount, an only very slight dependence on the surface coverage was observable, which indicated that the energetic heterogeneity of adsorption sites is significantly lower in the present adsorbent than in γ-Al_2O_3. Easy extrapolation to zero coverage allowed to obtain the limiting isosteric heat of adsorption, $Q_{a,0}$, with a reproducibility of ±0.1 kcal/mol between different runs; the averages for each adsorbate are reported in Table 3.

Table 3. Gas-chromatographic heats of adsorption at zero surfaces coverage (mean values).

Adsorbate	$Q_{a,0}$ [kcal/mol]	Adsorbate	$Q_{a,0}$ [kcal/mol]
Cyclohexane	9.3	CH_2Cl_2	9.1
Cyclohexene	11.1	CH_3-CCl_3	8.6
Benzene	11.6	$CH_2Cl-CHCl_2$	12.9
CCl_4	9.4	CH_2Cl-CH_2Cl	11.5
$CHCl_3$	9.8		

The heats of adsorption on silica-gel of the cyclic hydrocarbons are somewhat higher than those found on γ-Al_2O_3 [3], MgO [4] and ZrO_2 [5], but show a similar trend: on passing from cyclohexane to cyclohexene, $Q_{a,0}$ increases by a significantly larger amount than passing from cyclohexene to benzene. The first increment in $Q_{a,0}$, corresponding to a specific interaction of the polar surface hydroxyls with the olefinic double bond, amounts to 1.8 kcal/mol on silica-gel, which is not far from the value of 1.4 kcal/mol, common to the three other adsorbents. The second increment amounts to 0.5, 0.6, 0.9 and 0.4 kcal/mol with SiO_2, γ-Al_2O_3, MgO and ZrO_2, respectively; thus, with each of these adsorbents, the total increment from cyclohexane to benzene (which reflects the interaction with the resonance-stabilized aromatic π-electron system) never deviates by more than 10% from the average (2.1 kcal/mol).

As for the chlorinated compounds, the present results can be discussed as in the previous paper [1], taking into account both the contribution from electrostatic interaction of the surface electric field with the adsorbate molecular dipoles and the orientation of the adsorbed molecules. For example, the increment in $Q_{a,0}$ from CCl_4 to $CHCl_3$ (although smaller than in the case of γ-Al_2O_3) may be considered as indicating the electrostatic contribution, and denoting an "upright" position of the adsorbed $CHCl_3$ molecules, whereas for CH_3-CCl_3 an inclined position of the molecules is suggested by the low $Q_{a,0}$ value.

However, some differences from previous results can be observed, the most important of which concerns $CH_2Cl-CHCl_2$: a single chromatographic peak was always detected with this adsorbate, instead of the two separate peaks observed on γ-Al_2O_3, thus indicating that only one kind of orientation is now experienced by the adsorbed molecules. Further, from the remarkably high value of the adsorption heat, it may be inferred that this orientation involves the relatively large dipoles of molecules in the *trans* configuration.

Also 1.2-dichloroethane showed only one peak and has a somewhat large adsorption heat; it seems likely that the adsorbed molecules are mainly in the *gauche (skew)* configuration.

Anyhow, the observed differences between some of the present results on silica-gel and those on γ-Al_2O_3 might well be caused by pronounced changes in the porous texture of the adsorbents, such as the distribution of pore sizes and volumes and especially the possible occurrence of submicropores. The large difference in surface area gives just a first indication, but a more detailed investigation in this direction seems desirable.

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