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THERMODYNAMICS OF ADSORPTION OF ORGANICS ON A COBALT-MODIFIED SOLID OBTAINED FROM COLLOIDAL SILICA

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SUMMARY

Adsorption of various organics, including *n*-alkanes, cyclohexane, benzene and halomethanes, on the solid surface obtained from colloidal silica was studied by gas–solid chromatography (GSC). Adsorption experiments, ranging from zero surface coverage and to finite concentration, were performed in the temperature region from 333 to 443 K. In order to reduce surface inhomogeneity, a modified material was prepared by controlled surface silanol proton–Co²⁺ ion exchange and its adsorption properties were also investigated by GSC. Comparing the values for the standard free energy change for adsorption at zero coverage for all adsorbates used, it can be deduced that the modification procedure diminished the intensity of adsorption and so enhanced the homogeneity of the solid surface. Adsorption isotherms were obtained using the elution by characteristic point technique and the data were fitted to the BET equation. Thermodynamic parameters for adsorption in the finite concentration region were determined and are discussed in terms of the surface coverage.

INTRODUCTION

Silica is one of the most frequently used adsorbents in gas–solid chromatography (GSC), no matter whether selective separation of gases and low boiling organic compounds are concerned, or the determination of thermodynamic parameters in order to get a better insight into the adsorption process. The main disadvantage of a polar adsorbent is its surface inhomogeneity, resulting in peak asymmetry, too long retention times and reduced column efficiency. The available literature indicates that both thermal treatment^{1–3} and different sorts of chemical modifications^{4–7} of silica reduce or eliminate some of the active adsorption sites and result in a more uniform surface.

Rowan, Jr. and Sorrell⁴ have shown that a modified adsorbent enabling increased resolution and reduced peak asymmetry can be produced by the reaction of an alcohol or a chlorosilane with the surface hydroxyls of the silica gel. Coating of

porous silica beads (Porasil C) with different inorganic salts was performed⁵ in order to establish optimum conditions for selective separations. The most effective separation of aliphatic compounds was obtained with either sodium sulphate or sodium phosphate as the coating salt, while for benzenes cobalt(II) sulphate was found to be superior to all other salts studied. Cooke *et al.*⁶ modified the silica surface by coating it with chlorides of Ca^{2+} , Mn^{2+} , Co^{2+} and Zn^{2+} . The modified adsorbents yield more symmetrical elution peaks and decreased retention times, which reduces analysis times and provides more accurate thermodynamic adsorption data.

A quite different modification treatment has been reported from this Laboratory⁷. The surface of the solid material obtained from colloidal silica of very high purity has been altered by ion exchange of alkali-metal ions, resulting in reduced retention times of the organics investigated.

Continuing previous investigations on the adsorption process occurring at the surface of silica, a new adsorbent was prepared by controlled surface silanol proton- Co^{2+} ion exchange applied to the solid obtained from colloidal silica. The adsorption properties of both the modified and the unmodified adsorbents were investigated by GSC. The modification was performed in order to reduce the surface inhomogeneity of the starting material, and Co^{2+} was selected as a modifying agent because of its very important catalytic properties.

EXPERIMENTAL

Colloidal silica was obtained from liquid glass by an ion-exchange procedure described previously⁸. Coagulation of the colloidal material was carried out by adding to it 0.5 *M* sodium chloride at pH 10.4. Disperse phases were separated by filtration. The solid phase was then transferred to a polyethylene bottle containing 0.1 *M* hydrochloric acid solution and allowed to equilibrate for 24 h. The washing procedure was repeated and the pH of the solution after equilibration was 2.2, corresponding to the pH at the point of zero charge of fully protonated silica. The solid phase was separated by filtration and washed with doubly distilled water until no further reaction with chloride ions was observed. The material was dried, first in air and afterwards in an air oven at 383 K for 24 h. It was crushed, then sieved and a 0.149–0.210 mm fraction was used as an unmodified adsorbent ($\text{SiO}_2\text{-H}$) for column packing and, also, as a starting material for the modification procedure.

To exchange Co^{2+} for silanol protons, 2.5 g of the solid unmodified material were allowed to equilibrate with 25 ml of 0.01 *M* solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ for 2 h. In order to avoid formation of hydrolytic species of Co^{2+} , the pH of the prepared solution was 6.9. The equilibration procedure was repeated three times with a fresh portion of the solution. The solid phase was then separated by filtration, washed with doubly distilled water until no further reaction with sulphate ions was observed and dried in air. The modified adsorbent obtained, $\text{SiO}_2\text{-Co}$, was used as a column packing.

Bound Co^{2+} was extracted with a 2 *M* nitric acid solution at room temperature. Measurement of the concentration of the Co^{2+} in the nitric acid solution was carried out by atomic absorption spectrometry (AAS) using a Perkin-Elmer Model 6500 ICP. A value of 11.2 $\mu\text{mol Co}^{2+}$ per g SiO_2 was obtained.

The specific surface area of each adsorbent was determined using the three-point

nitrogen adsorption method with a BET calculation. Values found were 214 and 234 m²/g for SiO₂-H and SiO₂-Co samples, respectively. The amorphous structure of the materials was established by the X-ray method, using a Siemens Kristalloflex 4 instrument with CuK_α radiation.

The adsorption properties of the materials were examined using a Spectra Physics model 7100 research gas chromatograph with flame ionization detection (FID). Dry nitrogen was employed as the carrier gas. The column inlet pressure was measured by a mercury manometer, and the outlet pressure, assumed to be atmospheric, was measured by a precise barometer. All the other relevant parameters were measured and controlled with the precision required for physico-chemical measurements. Stainless-steel columns, 77 cm × 2.2 mm I.D., were cleaned with both polar and non-polar solvents prior to packing. After packing each column was conditioned overnight under a nitrogen flow at 523 K.

The organic adsorbates, obtained from various commercial sources, were of analytical grade and injected with a 10-μl Hamilton syringe. The system dead-time was assumed to be equal to the retention time of methane at the column temperature. Experiments were performed in the temperature region from 333 to 443 K.

The mass of the column packing, measured after the GSC experiments, was 1.490 and 1.610 g for the SiO₂-H and SiO₂-Co adsorbents, respectively.

RESULTS AND DISCUSSION

Zero surface coverage region

The adsorption of different organics on both the modified and the unmodified adsorbents was investigated in the linear part of the adsorption isotherms (Henry's law region), where lateral interactions between the adsorbed molecules on the surface can be neglected and the thermodynamic functions depend only on the adsorbate-adsorbent interactions. The attainment of the Henry's law region was indicated by the symmetry of the chromatographic peaks and by the constancy of the retention times measured over a significant range of sample sizes. Hence, the net retention volumes for a given adsorbate are independent of its gas phase concentration.

The distribution coefficient, K_s , in the Henry's law region is given by⁹

$$K_s = V_n/A_s \text{ (cm}^3 \text{ m}^{-2}\text{)} \tag{1}$$

where V_n (cm³) is the adsorbate net retention volume and A_s (m²) denotes the total surface area of the adsorbent in the column. Distribution coefficients for all the experimental temperatures and adsorbates used on the two adsorbents are given in Tables I and II.

The standard free energy change for adsorption under zero coverage conditions, $-\Delta G_a^0$, may be derived from⁹

$$-\Delta G_a^0 = RT \cdot \ln(p_{s,g} \cdot K_s / \pi_s) \text{ (kJ mol}^{-1}\text{)} \tag{2}$$

where $p_{s,g}$ is the adsorbate vapour pressure in the gaseous standard state (101 kPa) and π_s is the spreading pressure of the chosen surface standard state. Introducing a widely used definition for the surface standard state proposed by De Boer¹⁰, π_s becomes 0.338 mN m⁻¹.

TABLE I
DISTRIBUTION COEFFICIENTS, K_s ($\text{cm}^3 \text{m}^{-2}$), OF ADSORBATES ON $\text{SiO}_2\text{-H}$ ADSORBENT

Adsorbate	$T(K)$									
	333	353	363	373	383	393	413	423	433	443
<i>n</i> -Hexane	1.552	0.579		0.271		0.133				
<i>n</i> -Heptane			1.124	0.694	0.444	0.297				
Cyclohexane	1.224	0.499		0.249		0.127				
Benzene							0.465	0.318	0.225	0.159
Dichloromethane	1.224	0.579		0.297		0.155				
Chloroform		0.983	0.643	0.482		0.206				
Carbon tetrachloride		0.736	0.491	0.369		0.162				

At zero surface coverage, the standard enthalpy change for adsorption, $-\Delta H_a^0$, can be identified¹⁰ with the differential heat of adsorption, q_a^0 , and may be obtained from the temperature dependence of K_s according to:

$$d(\ln K_s)/d(1/T) = q_a^0/R = -\Delta H_a^0/R \quad (3)$$

Provided that $-\Delta H_a^0$ is temperature independent over the temperature region studied, eqn. 3 predicts a linear relationship between $\ln K_s$ and $1/T$. The $-\Delta H_a^0$ values were obtained using the method of least squares.

The standard entropy change for adsorption, ΔS_a^0 , may be calculated from the expression:

$$\Delta S_a^0 = (\Delta H_a^0 - \Delta G_a^0)/T \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (4)$$

Thermodynamic parameters for adsorption of all the adsorbates examined under zero coverage conditions are presented in Tables III and IV. According to the K_s values listed in Tables I and II, or more exactly from the corresponding $-\Delta G_a^0$ values (Tables

TABLE II
DISTRIBUTION COEFFICIENTS, K_s ($\text{cm}^3 \text{m}^{-2}$), OF ADSORBATES ON $\text{SiO}_2\text{-Co}$ ADSORBENT

Adsorbate	$T(K)$									
	333	353	363	373	383	393	413	423	433	443
<i>n</i> -Hexane	1.243	0.490		0.217		0.106				
<i>n</i> -Heptane			0.965	0.607	0.389	0.254				
Cyclohexane	1.048	0.425		0.199		0.097				
Benzene							0.352	0.225	0.168	0.130
Dichloromethane	0.986	0.442		0.216		0.115				
Chloroform		0.768	0.509	0.355		0.173				
Carbon tetrachloride		0.563	0.400	0.294		0.143				

TABLE III

STANDARD THERMODYNAMIC ADSORPTION PARAMETERS OF ADSORBATES UNDER ZERO COVERAGE CONDITIONS ON SiO₂-H

<i>Adsorbate</i>	<i>T</i> (K)	$-\Delta G_a^0$ (kJ mol ⁻¹)	$-\Delta H_a^0$ (kJ mol ⁻¹)	$-\Delta S_a^0$ (J mol ⁻¹ K ⁻¹)
<i>n</i> -Hexane	333	17.00	44.2 ± 0.1	82.1 ± 0.3
	353	15.13		
	373	13.62		
	393	12.03		
<i>n</i> -Heptane	363	17.56	52.7 ± 0.2	97.0 ± 0.1
	373	16.55		
	383	15.57		
	393	14.66		
Cyclohexane	333	16.34	40.7 ± 0.1	73.5 ± 0.5
	353	14.69		
	373	13.36		
	393	11.89		
Benzene	413	16.94	55.9 ± 0.1	94.1 ± 0.1
	423	16.02		
	433	15.15		
	443	14.23		
Dichloromethane	333	16.34	37.9 ± 0.0	65.5 ± 0.2
	353	15.13		
	373	13.92		
	393	12.54		
Chloroform	353	16.68	44.5 ± 0.3	78.7 ± 0.5
	363	15.87		
	373	15.41		
	393	13.47		
Carbon tetrachloride	353	15.83	43.2 ± 0.3	77.3 ± 0.4
	363	15.06		
	373	14.58		
	393	12.69		

III and IV), *n*-heptane exhibits more intensive interactions with both adsorbents investigated than does *n*-hexane. This is a consequence of the additional CH₂ group in the molecule of *n*-heptane, available for non-specific interaction with the surface. The increment in the standard free energy change of adsorption, $-\Delta G(-CH_2-)$, contributed by this extra CH₂ group, at 373 K is 2.93 and 3.19 kJ mol⁻¹ for the SiO₂-H and SiO₂-Co adsorbents, respectively. The value of 2.93 kJ mol⁻¹ for the unmodified adsorbent is in a good agreement with the values of 2.39 kJ mol⁻¹ at 433 K (see ref. 7) and 3.12 kJ mol⁻¹ at 373 K (see ref. 11) obtained previously for a similar silica adsorbent (unmodified material).

Cyclohexane is less strongly retained than the corresponding *n*-alkane with the same number of carbon atoms (*n*-hexane) on both adsorbents used (Tables III and IV), which can probably be explained by the existence of a "boat" structural isomer in addition to the "chair" configuration, preventing maximum adsorption.

TABLE IV

STANDARD THERMODYNAMIC ADSORPTION PARAMETERS OF ADSORBATES UNDER ZERO COVERAGE CONDITIONS ON SiO₂-Co

Adsorbate	<i>T</i> (K)	$-\Delta G_a^0$ (kJ mol ⁻¹)	$-\Delta H_a^0$ (kJ mol ⁻¹)	$-\Delta S_a^0$ (J mol ⁻¹ K ⁻¹)
<i>n</i> -Hexane	333	16.39	44.6 ± 0.1	84.7 ± 0.1
	353	14.64		
	373	12.94		
	393	11.29		
<i>n</i> -Heptane	363	17.10	52.8 ± 0.1	98.4 ± 0.0
	373	16.13		
	383	15.14		
	393	14.14		
Cyclohexane	333	15.91	42.9 ± 0.0	81.3 ± 0.1
	353	14.22		
	373	12.67		
	393	11.00		
Benzene	413	15.99	51.7 ± 0.4	86.6 ± 0.4
	423	14.80		
	433	14.10		
	443	13.48		
Dichloromethane	333	15.74	38.9 ± 0.0	69.7 ± 0.0
	353	14.33		
	373	12.93		
	393	11.56		
Chloroform	353	15.96	42.7 ± 0.0	75.8 ± 0.1
	363	15.17		
	373	14.47		
	393	12.89		
Carbon tetrachloride	353	15.04	39.7 ± 0.1	69.3 ± 0.5
	363	14.44		
	373	13.88		
	393	12.70		

Since benzene retention times in the temperature range 333–393 K exceed 1 h, its adsorption was studied in the temperature range 413–443 K. However, although the standard enthalpy change for adsorption of *n*-hexane was determined in different temperature regions, it can be supposed that a linear relationship between $\ln K_s$ and $1/T$ is valid for the extended region from 333 to 443 K, allowing a comparison of the interactions of *n*-hexane and benzene with the adsorbent surface. The higher negative $-\Delta H_a^0$ value for benzene, compared with *n*-hexane, and hence the more intensive interaction with the surfaces of both adsorbents, is a consequence of the π -electron bonds existing in the aromatic molecule of benzene. Specific interaction between the π -electrons of benzene and the surface hydroxyl groups is to a certain extent similar to an hydrogen bond¹². The rôle of the specific part of the interaction can be evaluated by considering the differential standard free energy of adsorption, $-\Delta(\Delta G^0)$ ¹¹

$$-\Delta(\Delta G^0) = RT \cdot \ln[K_s(C_6H_6)/K_s(nC_6)] \text{ (kJ mol}^{-1}\text{)} \quad (5)$$

where $K_s(nC_6)$ is the distribution coefficient for *n*-hexane at the temperature T , and $K_s(C_6H_6)$ is that for benzene, extrapolated to the same temperature. The $-\Delta(\Delta G^0)$ values obtained are 6.78 and 6.21 kJ mol⁻¹ for SiO₂-H and SiO₂-Co, respectively.

Concerning the data obtained for halomethanes, it is clear that chloroform interacts more strongly with the surface of the adsorbent than does carbon tetrachloride or dichloromethane. For silica as well as for other adsorbents¹³⁻¹⁵, the intensity of adsorption does not follow the trend normally expected on the basis of the number of chlorine atoms, boiling point or dipole moment. Chloroform exhibits a certain specific interaction not only because of its dipole moment ($\mu = 3.33 \cdot 10^{-30}$ C m) but also due to its extreme asymmetry, in contrast to the symmetrical molecules of dichloromethane ($\mu = 5.33 \cdot 10^{-30}$ C m) and carbon tetrachloride ($\mu = 0.00$ C m).

From the data obtained (Tables I-IV) it can be concluded that for all adsorbates used the adsorption process is less intensive on the modified than on the unmodified adsorbent. This result was expected since, in the process of cobalt-modification, active protons from surface silanol groups were exchanged with Co²⁺ (ref. 16), reducing the number of surface hydroxyls that can act as active adsorption centres. The reduction in the intensity of the interactions with the modified silica, in combination with a significant reduction in the asymmetry of the chromatographic peak shape, implies a reduction in the heterogeneity of this material.

Finite coverage region

At finite coverages the surface adsorption results in non-linear isotherms where the distribution coefficients are dependent on the adsorbate concentration in the gas phase.

Adsorption isotherms for all the adsorbates investigated were obtained using the elution by characteristic point (ECP) technique detailed elsewhere¹⁷. In ECP measurements it is important to assure that the effect of non-ideality is small in comparison with non-linearity¹⁷. It is checked by noting that the self-sharpening side of the peak is vertical and that, when peaks of different sizes are superimposed, the peak maxima lie on the common envelope of the diffuse sides.

The amount of probe adsorbed, a , at the temperature T , according to the ECP procedure, can be obtained from¹⁷

$$a = (jp_o F_{jy_o} S_a y_o) / (hvRTm) \text{ (mol g}^{-1}\text{)} \tag{6}$$

where j is the James-Martin compressibility factor, p_o (Pa) the outlet column pressure, y_o the mole fraction of the adsorbate in the gas phase at the column outlet, S_a (cm²) the chart area bounded by the GS adsorption envelope of the peak maxima and by the axis at time $t = t_M$, where t_M is the system dead time, h (cm) the peak height, v (cm min⁻¹) the chart speed, R the gas constant, T (K) the experimental temperature and m (g) is the total weight of adsorbent in the column. The term F_{jy_o} , representing the total volume flow-rate, measured at the column outlet, through a zone containing a mole fraction y_o , can be expressed by¹⁸

$$F_{jy_o} = F_o(1 + k) / [1 + k(1 - jy_o)] \text{ (ml min}^{-1}\text{)} \tag{7}$$

where F_o (ml min⁻¹) is the total volume flow-rate at $y_o = 0$, measured at the column

outlet, and k is the mass distribution coefficient of the adsorbate. Using F_{jy_0} , a correction for the sorption effect was introduced. It cannot be neglected because the mole fraction, for all adsorbates used, in the gas phase exceeds 0.01 (ref. 17).

The vapour pressure, p (in Pa), corresponding to the amount of the probe adsorbed, a , is given by¹⁹

$$p = (m_a v R T h) / (S F_c) \quad (8)$$

where m_a (mol) is the known amount of sample injected, S (cm²) is the peak area and F_c is the column flow-rate at the column temperature, T , corrected for pressure drop and for the presence of water in the soap-bubble flowmeter.

The correction for gas phase imperfection can be neglected because in this work the mean column pressure did not exceed $1.01 \cdot 10^6$ Pa (10 atm)²⁰. The adsorption isotherms obtained are represented in the form $a = f(p/p_a)$, where p_a is the vapour pressure of the sorbate liquid calculated by the Antoine equation²¹.

Experimental adsorption isotherms were fitted to the BET equation²²

$$a = \frac{a_m C (p/p_a)}{(1 - p/p_a) [1 + (C - 1) (p/p_a)]} \quad (9)$$

where a_m (mol g⁻¹) is the monolayer capacity, and C is a constant correlated with the heat of adsorption. In order to determine a_m and C , each experimental isotherm was

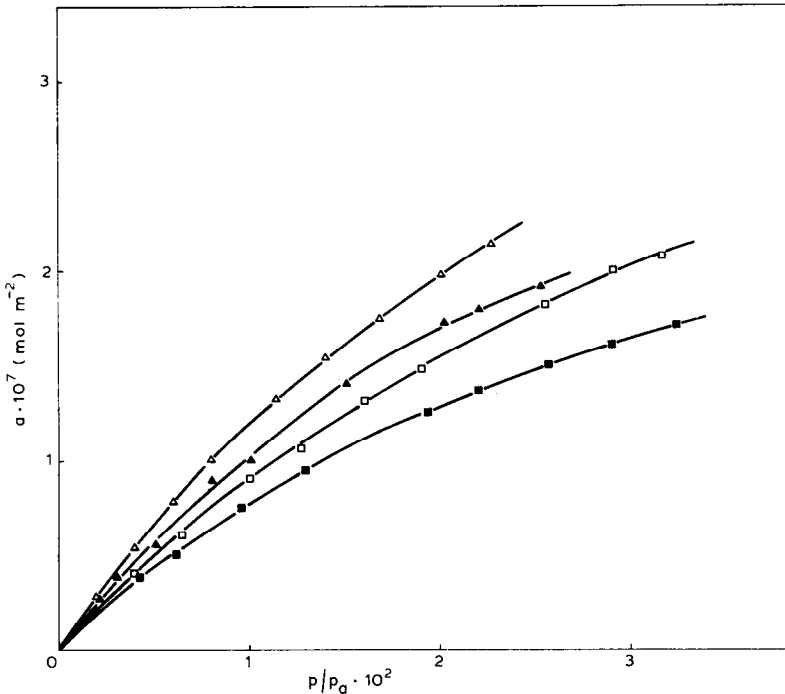


Fig. 1. Adsorption isotherms for *n*-hexane on the SiO₂-H adsorbent. The solid lines represent BET fits. T (K): 333 (Δ); 353 (\blacktriangle); 373 (\square); 393 (\blacksquare).

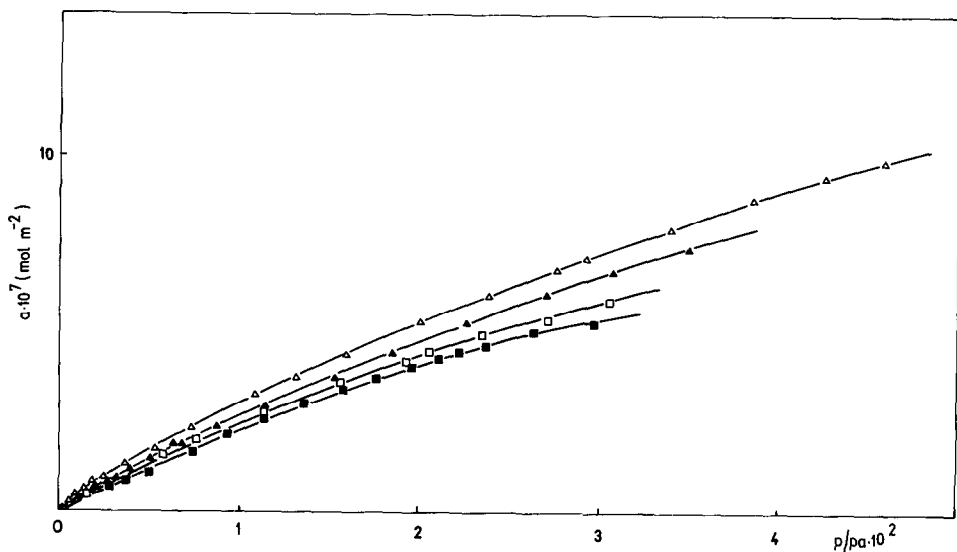


Fig. 2. Adsorption isotherms for chloroform on the SiO₂-H adsorbent. The solid lines represent BET fits T (K): 353 (Δ); 363 (\blacktriangle); 373 (\square); 393 (\blacksquare).

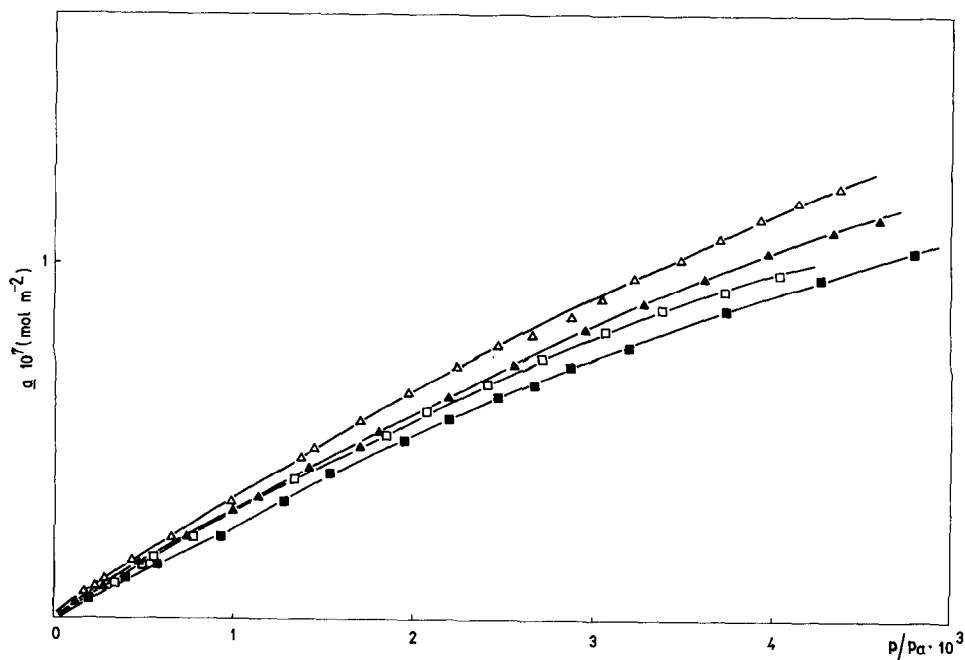


Fig. 3. Adsorption isotherms for benzene on the SiO₂-H adsorbent. The solid lines represent BET fits T (K): 413 (Δ); 423 (\blacktriangle); 433 (\square); 443 (\blacksquare).

reduced to the linear form of the BET equation applied to the whole p/p_a range experimentally utilized. The constants a_m and C were obtained using the least squares method.

Figs. 1–3 present examples of the isotherms computed for *n*-hexane, chloroform and benzene, each representing a class of organics, on the $\text{SiO}_2\text{-H}$ adsorbent. Similar patterns are obtained for the cobalt-modified variety. The BET fit is represented by the solid line. The BET constants, a_m and C , for all systems studied are compiled in Table V. It is obvious (Figs. 1–3) that the adsorption process for *n*-hexane, chloroform and benzene for the given coverage range can be very well described by the BET model. Due to non-coincidence in the diffuse sides of the peaks at higher coverages, the ECP technique cannot be used to obtain multilayer adsorption data.

In order to get a better insight into the adsorption process in the finite coverage

TABLE V
BET CONSTANTS, a_m (mol m^{-2}) AND C , FOR ADSORBATES ON $\text{SiO}_2\text{-H}$ AND $\text{SiO}_2\text{-Co}$

Adsorbate	$T(K)$	$\text{SiO}_2\text{-H}$		$\text{SiO}_2\text{-Co}$	
		$a_m \cdot 10^7$	C	$a_m \cdot 10^7$	C
<i>n</i> -Hexane	333	5.19	29.35	1.45	149.11
	353	3.70	40.05	1.96	73.89
	373	4.55	24.55	2.52	42.73
	393	3.23	31.61	2.44	38.60
<i>n</i> -Heptane	363	7.59	13.52	1.71	85.08
	373	7.14	13.08	1.91	65.25
	383	6.19	14.21	1.79	37.35
	393	3.84	22.32	2.23	41.00
Cyclohexane	333	6.69	12.41	2.28	45.51
	353	5.23	14.85	2.54	31.53
	373	5.12	13.02	3.16	21.30
	393	4.59	12.31	—	—
Benzene	413	3.88	99.84	8.68	18.61
	423	3.49	101.35	9.04	16.51
	433	3.02	115.28	11.65	11.33
	443	3.52	84.88	8.89	15.55
Dichloromethane	333	10.30	36.14	6.39	54.21
	353	16.31	18.09	3.94	99.60
	373	—	—	5.39	51.92
	393	11.08	22.51	5.23	47.39
Chloroform	353	23.9	13.50	4.56	66.21
	363	19.5	15.77	5.71	40.79
	373	15.7	18.68	5.70	37.14
	393	13.0	22.79	6.10	30.62
Carbon tetrachloride	353	9.41	9.48	2.97	43.21
	363	8.85	10.31	3.64	29.93
	373	—	—	3.32	32.70
	393	13.69	4.52	4.96	16.96

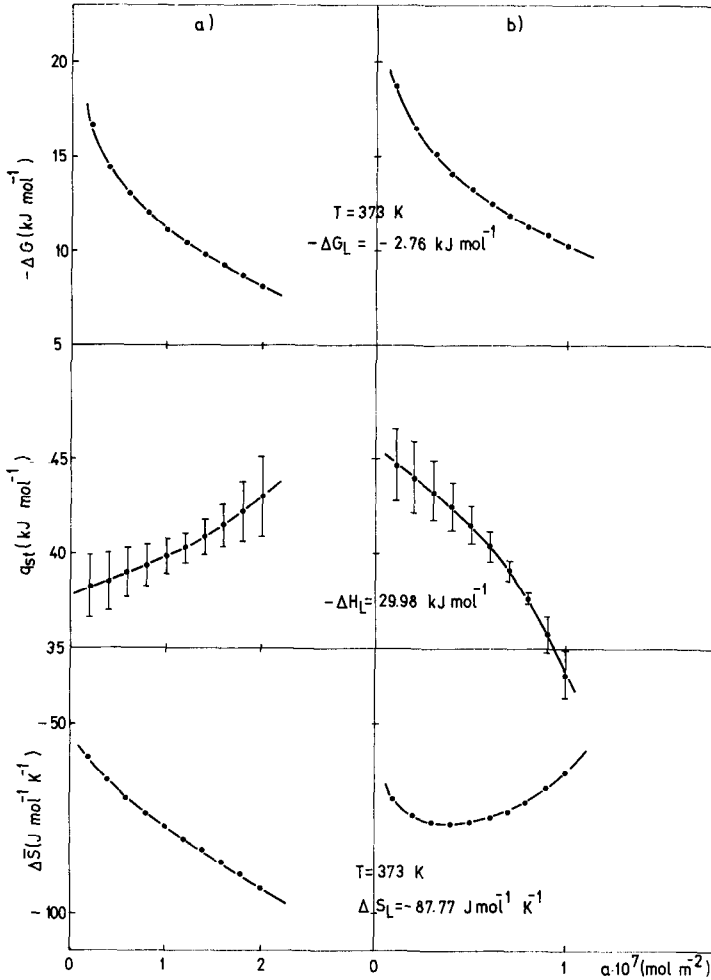


Fig. 4. Dependence of thermodynamic adsorption parameters of *n*-hexane on the surface coverage for: (a) SiO₂-H adsorbent and (b) SiO₂-Co adsorbent; $-\Delta G_L$, $-\Delta H_L$ and ΔS_L are the corresponding parameters for pure liquid *n*-hexane.

region, thermodynamic parameters of adsorption were determined. Assuming ideal gas behaviour, the partial molar free energy of adsorption was determined from each isotherm at the given amount of probe sorbed, a , from²³

$$\Delta \bar{G} = RT \cdot \ln(p/p_{s,g.}) \text{ (kJ mol}^{-1}\text{)} \tag{10}$$

using linear interpolation to calculate the vapour pressure, p , at the coverage in question. Here, $\Delta \bar{G}$ represents the change in free energy of adsorption as 1 mol of adsorbate passes from the vapour at unit fugacity to the surface at the coverage in question²³.

The isosteric heat of adsorption, q_{st} , for the given a can be calculated from²³

$$q_{st} = - [\partial(\Delta \bar{G}/T)/\partial(1/T)]_a \text{ (kJ mol}^{-1}\text{)} \tag{11}$$

by fitting the values of $(\Delta\bar{G}/T)$ at the given a to a linear least squares function in $1/T$. The partial molar entropy change for adsorption was obtained in the usual way:

$$\Delta\bar{S} = -(q_{st} + \Delta\bar{G})/T \text{ (J mol}^{-1} \text{ K}^{-1}\text{)} \quad (12)$$

Figs. 4–6 present the thermodynamic parameters of adsorption of *n*-hexane, chloroform and benzene on the $\text{SiO}_2\text{-H}$ and $\text{SiO}_2\text{-Co}$ adsorbents as a function of the surface coverage. The values of $-\Delta G_L$, $-\Delta H_L$ and ΔS_L are the corresponding parameters for pure liquid adsorbate.

The decrease of $-\Delta\bar{G}$ (Figs. 4–6) with increasing surface coverage indicates that

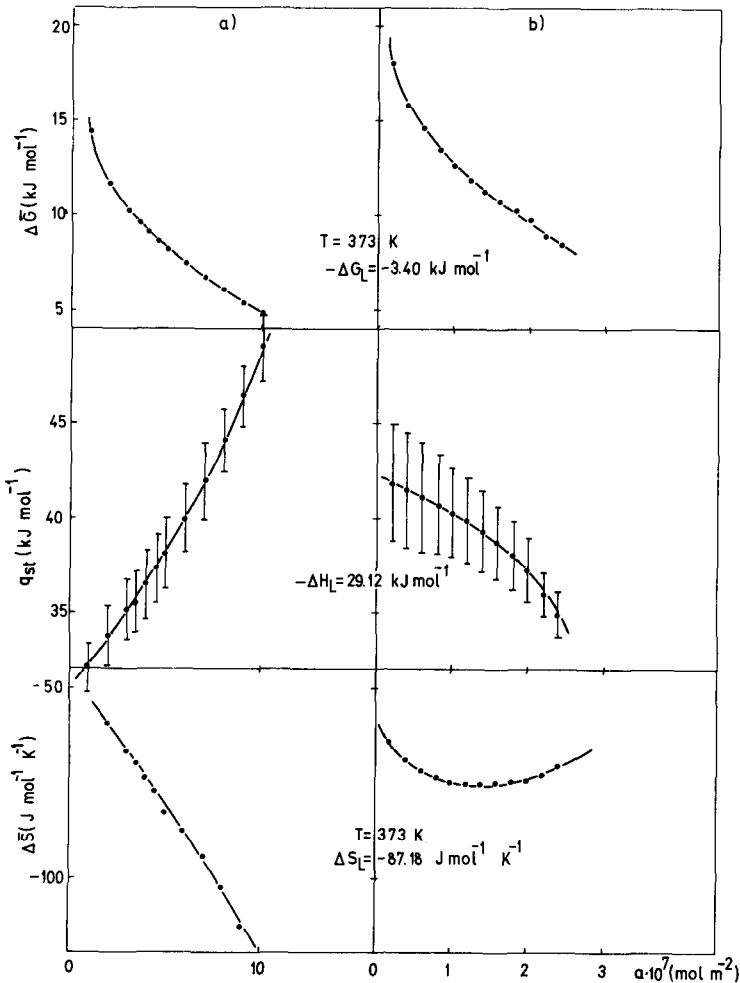


Fig. 5. Dependence of thermodynamic adsorption parameters of chloroform on the surface coverage for: (a) $\text{SiO}_2\text{-H}$ adsorbent and (b) $\text{SiO}_2\text{-Co}$ adsorbent; $-\Delta G_L$, $-\Delta H_L$ and ΔS_L are the corresponding parameters for pure liquid chloroform.

low surface coverages are preferred from the energy point of view. Also, as expected, all adsorbates presented show a non-liquid-like structure for the range of surface coverage studied. Errors (as standard deviations) in the q_{st} values were calculated and represented by the error bars in Figs. 4-6. The errors are of the usual order of magnitude for least squares treatment of eqn. 11. Due to somewhat larger errors at the initial part of the q_{st} plots (from 1.5 kJ mol^{-1} for chloroform on the $\text{SiO}_2\text{-H}$ adsorbent to 3.3 kJ mol^{-1} for benzene on the $\text{SiO}_2\text{-Co}$ adsorbent), the shape of these curves at low surface coverages is not quite certain. It can be concluded, however, from Figs. 4-6 that the trend in q_{st} is different for the modified and the unmodified adsorbents. Further, Figs. 4-6 indicate that for adsorption on the unmodified adsorbent there is an increase in q_{st} which may possibly yield a maximum corresponding to the coverage at

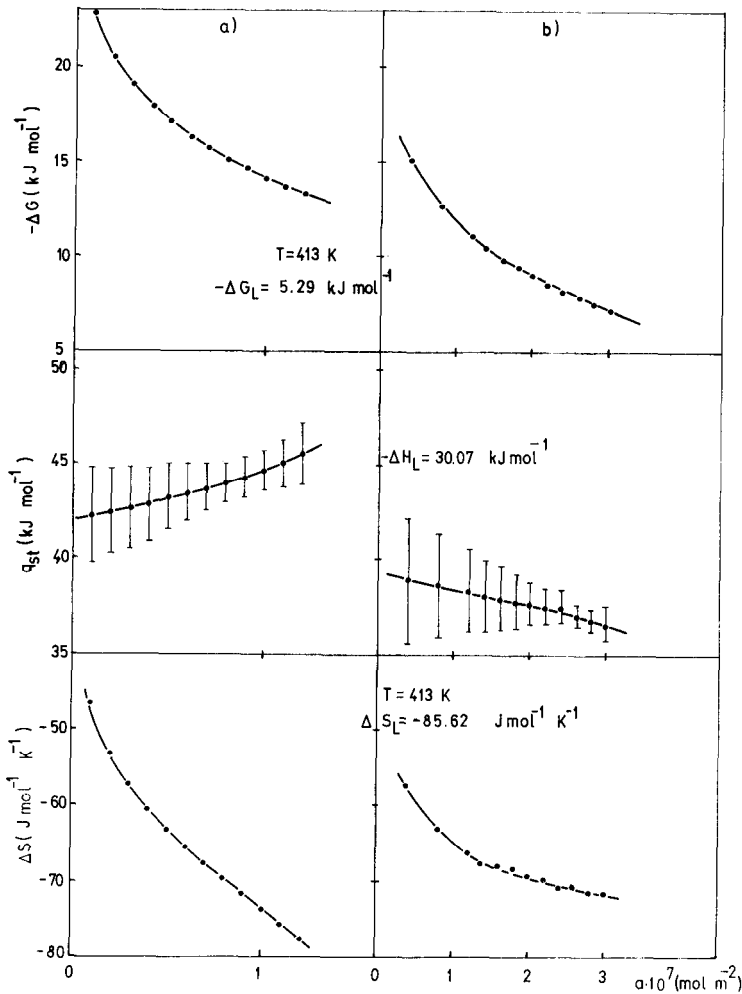


Fig. 6. Dependence of thermodynamic adsorption parameters of benzene on the surface coverage for: (a) $\text{SiO}_2\text{-H}$ adsorbent and (b) $\text{SiO}_2\text{-Co}$ adsorbent; $-\Delta G_L$, $-\Delta H_L$ and ΔS_L are the corresponding parameters for pure liquid benzene.

which the most energetically favourable sites, probably originating from strong, localized sorbate-sorbent interactions²³, are created. Similar behaviour was observed in the case of adsorption of hexan-1-ol and butan-1-ol on cotton cellulose, which can be explained by the ability of cellulose to form strong localized sorbate-sorbent interactions through hydrogen bonding²³. However, the increase in q_{st} with increasing surface coverage for the adsorption of alkan-1-ols on graphitized carbon black was attributed to the creation of energetically favourable sites by sorbate-sorbent interactions²⁴. At the same time, the minimum in $\Delta\bar{S}$, for the case of adsorption on the unmodified adsorbent, may be due to a decrease in configurational entropy²³. In the case of adsorption on the modified adsorbent, the minimum in $\Delta\bar{S}$ is quite obvious, showing that the modification procedure applied reduces the number of active adsorption sites, yielding a more homogeneous surface.

The lack of a maximum in q_{st} on the cobalt-modified solid may be ascribed to the reduced number of high energy adsorptive sites, which upon modification are converted into less active cobalt-form sites.

The dependence of the thermodynamic parameters in the finite concentration region on the surface coverage for all other adsorbates used has the same pattern as in Figs. 4-6.

Further increase in the surface coverage and, hence, a better insight into the adsorption process in the finite coverage region on both the modified and the unmodified adsorbents could not be attained due to the effects of non-ideality. Nevertheless, the thermodynamic results presented show that the modification procedure applied here to the fully protonated silica, using Co^{2+} to exchange the active protons from the surface silanol groups, leads to a less active adsorbent with a more homogeneous surface.

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