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GRAVIMETRICALLY MEASURED ISOTHERMS OF ADSORPTION OF BENZENE, *n*-HEXANE AND CYCLOHEXENE ON DIFFERENT POROUS SILICA GELS

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Abstract

The isotherms of adsorption-desorption of the vapour of benzene, cyclohexene and *n*-hexane on different porous silica gels were measured gravimetrically. For all the adsorbates, the amount of vapour condensed in the adsorbent pores is significantly greater than the amount adsorbed. The isotherms of all the adsorbates are linear in a wide range of relative pressures.

Keywords: adsorption, capillary condensation, gravimetric method, McBain microbalance

Introduction

It was stated earlier that the physical adsorption of the vapour of substances characterized by molecular sizes much smaller than the cross-section of the pores proceeds in a similar way on porous surfaces as it does on flat surfaces [1, 2]. The number of moles of vapour adsorbed by unit mass of porous adsorbent depends on the cross-section of the pores and on the size and geometric structure of the molecules adsorbed [3]. Dubinin and co-workers [4–8] divided adsorbents into three groups on the basis of their porous structure, and, with regard to their adsorption abilities, divided them into the following two groups: adsorbents characterized by a higher adsorption potential, which results from the interaction of the closely situated pore walls, and macroporous adsorbents, in which an effect of this kind does not occur. A division of this nature is controversial, because the rise in adsorption potential depends on the size and geometric structure of the molecules adsorbed. The influence of porosity upon the sorption abilities of a vapour (especially for light hydrocarbons) is an interesting problem, not only because we have a chance to examine the process of adsorption and the structures of adsorbents and catalysts [9–14], but also because of the possibility of using them as collectors to store gases and vapours of light hydrocarbons at elevated pressure [15–17]. Neither of these aspects has yet been examined definitively and research is continuing.

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The aim of the present paper is to determine the influence of the cross-section of the pores of silica gel upon the sorption abilities of the vapour of benzene, cyclohexene and *n*-hexane.

Experimental

Materials, experimental procedure and equipment used

Silica gel Si40, Si60 and Si100 (Merck) grain fraction 0.2–0.5 mm were used in this work. The silica gel was dried at 200°C for 4 h before use in measurements. The specific surfaces (S_v) of the silica gels were 793 for Si40, 522 for Si60 and 343 $m^2 g^{-1}$, for Si100, and the radii of their pores (d_p) were 2.1, 3.3 and 5.9 nm, respectively. The specific surfaces and diameters of their pores were calculated on the basis of measured adsorption-desorption isotherms for nitrogen, assuming the cross-section of the nitrogen molecule, ω_o, to be 0.16 $nm^2 mol^{-1}$.

The adsorption-desorption isotherms for nitrogen were measured with a Sorptomat (Carlo-Erba), while the adsorption-desorption isotherms for the vapour of the adsorbates used were measured gravimetrically in an apparatus with a McBain microbalance (Fig. 1). The adsorbates (pure for analysis) were dried

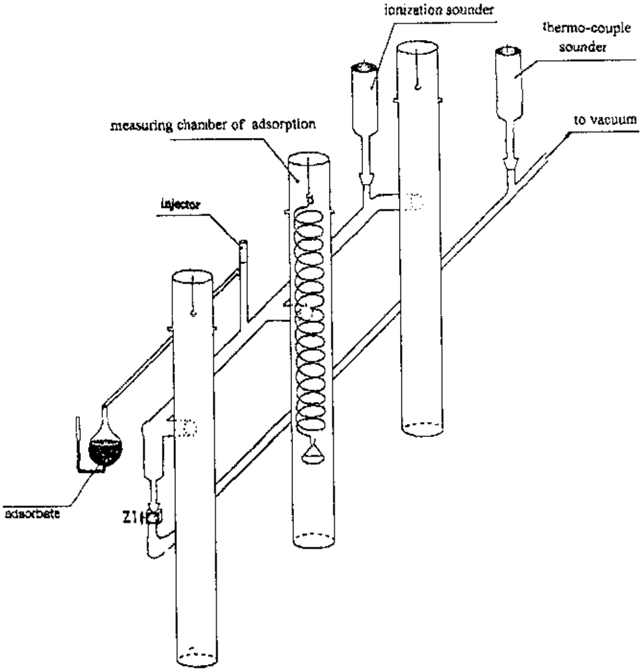

Fig. 1 Schematic diagram of the adsorption apparatus for measurements of adsorption-desorption isotherms from the vapour phase on solid surfaces

with A4 molecular sieve which had been dried previously for 6 h at 500°C. Silica gels prepared in the above way were used for adsorption and desorption measurements on the vapour of benzene, cyclohexene and *n*-hexane.

Discussion

Adsorbates differing slightly in the surface areas occupied by their adsorbed molecules (ω_0 for *n*-hexane=0.48, for cyclohexane=0.46 and for benzene= 0.40 nm^2 mol^{-1}) [18] were chosen for examination. The adsorption energies of the adsorbates used result from dispersive interactions. Despite the same number of carbons in the three molecules, differences should appear in their adsorption energies because of their different dispersive interactions. Benzene and cyclohexene interact with the adsorbent surface by means of π-electrons (of different densities), whereas *n*-hexane interacts with electric dipoles induced by the electrostatic field on the adsorbent surface [19].

Figures 2–4 illustrate the influence of the pore diameter of the silica gels used upon the adsorptions of the adsorbates examined (light symbols). It can be seen

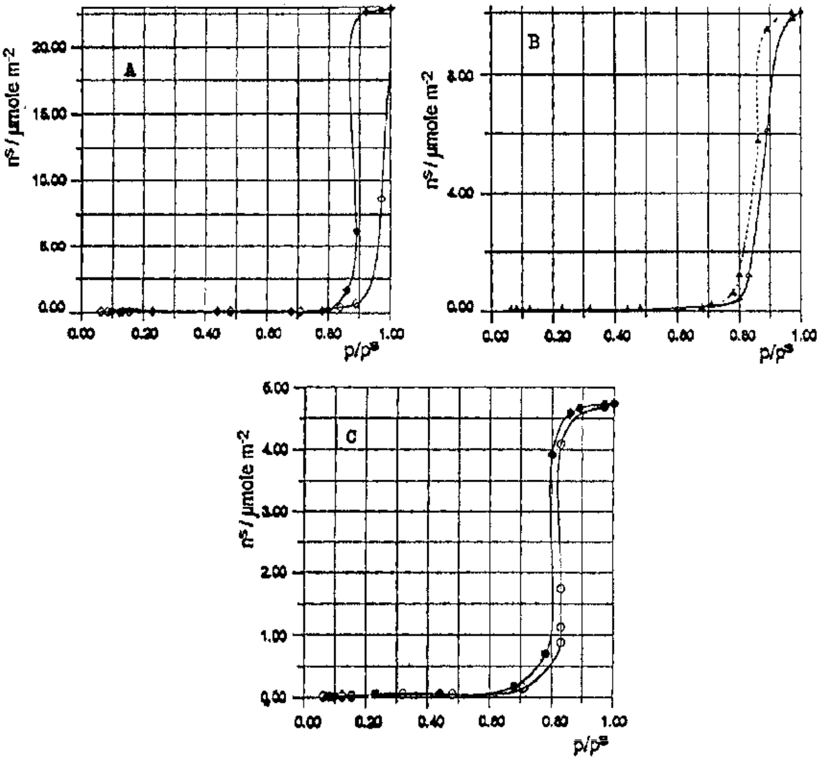

Fig. 2 Adsorption (light symbols) and desorption (dark symbols) isotherms for *n*-hexane vapour on different Merck silica gels: A – Si100, B – Si60 and C – Si40

that their adsorption is small, and proceeds linearly in a wide range of relative vapour pressures (p/p_s, where p denotes the equilibrium pressure, and p_s denotes the pressure of saturated vapour at the temperature of measurement). This is the reason why the ranges of relative pressures in which capillary condensation takes place are narrow.

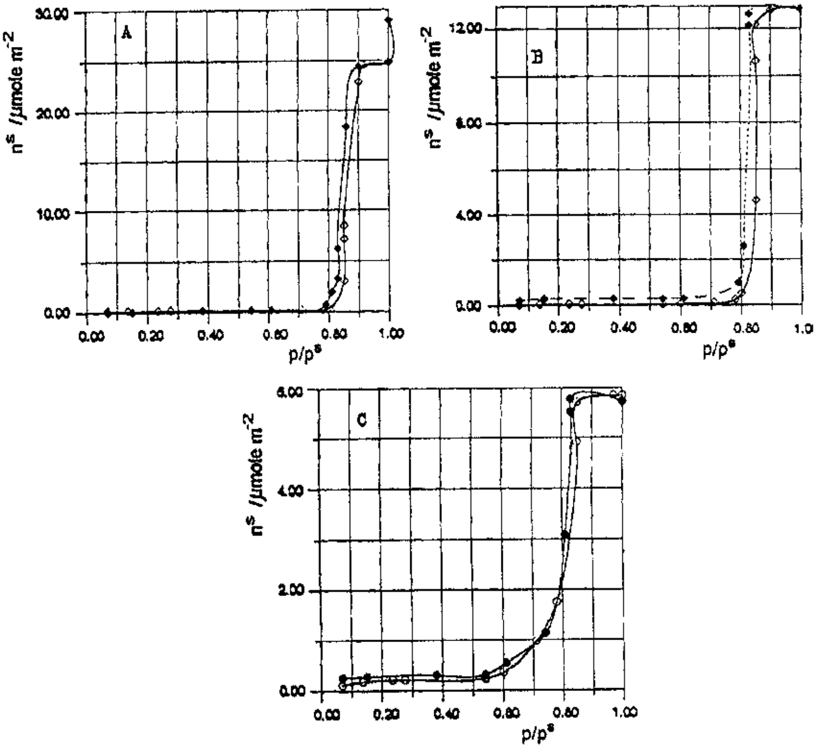

Fig. 3 Adsorption (light symbols) and desorption (dark symbols) isotherms for cyclohexene vapour on different Merck silica gels: A – Si100, B – Si60 and C – Si40

As may be seen in Figs 3C and 4C, the desorption curves for benzene and cyclohexene (dark symbols) on narrow-pore silica gel (Si40) nearly agree with the adsorption isotherms. Such a situation indicates that the adsorption on this adsorbent proceeds similarly to that on a flat surface. Moreover, Figs 2–4 reveal that the hysteresis loops of all these adsorbates on other silica gels are narrow and similar to one another. An exception is the much wider hysteresis loop of *n*-hexane on silica gel Si100.

According to De Boer's [20] theorem, such a shape of the hysteresis loop in adsorption-desorption isotherms arises from open capillaries with various configurations of their cross-sections (circular, triangular, square, and so on). In such capillaries, condensation sometimes initially occurs along their internal angles until a cylindrical meniscus, the result of the joining of angular meniscuses, appears. Further condensation takes place until fhe filling-up of the pores is completed, slightly changing the relative pressure (p/p_s). Assuming that such a process of capillary condensation is correct, the narrow hysteresis loop presented in Figs 2B, 2C, 3A, 3B, 4A and 4B may be explained in the following way: when the angle meniscuses join, the capillaries are filled with liquid adsorbates. Capillary condensation in liquid circular capillaries plays only a minimal part in the process. A narrow hysteresis loop formed in the adsorption-desorption isotherms for n-hexane vapour on Si40 may be explained in a similar way. On adsorbing, the n-hexane molecules direct themselves in parallel along their longest axis to the adsorbent surface; the process takes place inside the capillaries too. Hence, the layer arising from adsorbed n-hexane in the adsorbent pores forms meniscuses along the internal angles of the capillaries; when these join together, the meniscuses fill the capillaries (there is no condensation in liquid circular capillaries.

The above considerations are proved by the dependences of the differential free sorption energies ($-\Delta G$) and the number of moles of hydrocarbons sorbed (n^s) in Fig. 5. To calculate these dependences, the following equation was used [21]:

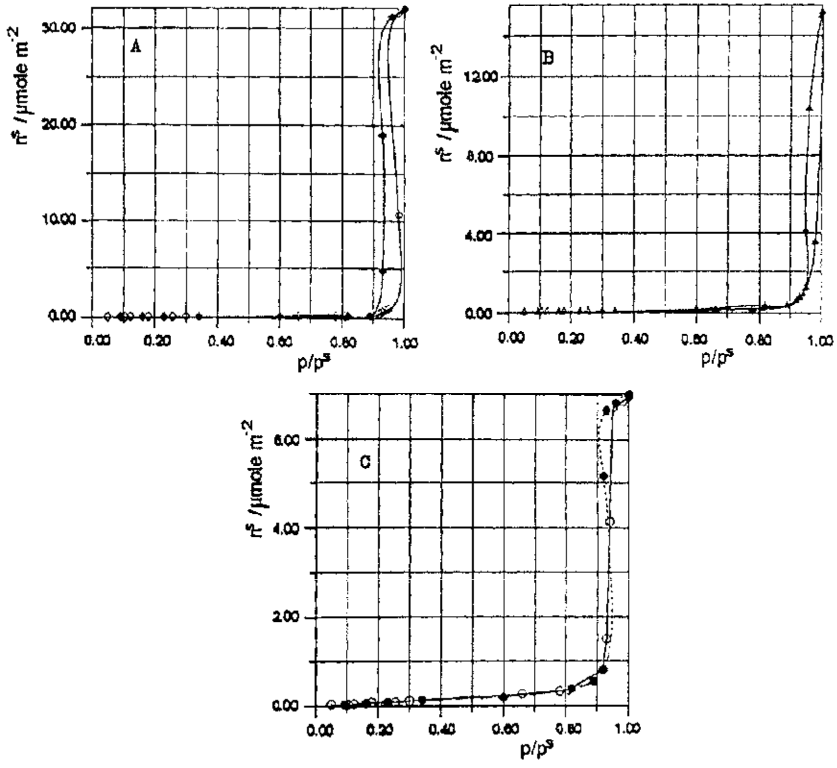

Fig. 4 Adsorption (light symbols) and desorption (dark symbols) isotherms for benzene vapour on different Merck silica gels: A – Si100, B – Si60 and C – Si40

$$-\Delta G = 2.303\ RT\log\left(\frac{p}{p_{\mathrm{s}}}\right) \tag{1}$$

where p is the equilibrium pressure, and p_{s} is the saturated vapour pressure at the temperature of the measurements.

The function ΔG *vs.* n^{s} for the examined adsorbents decreases linearly while the quantity of hydrocarbon adsorbed ($n_{\mathrm{a}}^{\mathrm{s}}$) increases until it reaches the value p/p_{s} corresponding to the beginning of the hysteresis loop (Fig. 5). Further adsorption of the vapour of the adsorbates takes place at the fixed values of $\Delta G(n^{\mathrm{s}})$ which correspond to their capillary condensation in the adsorbent pores.

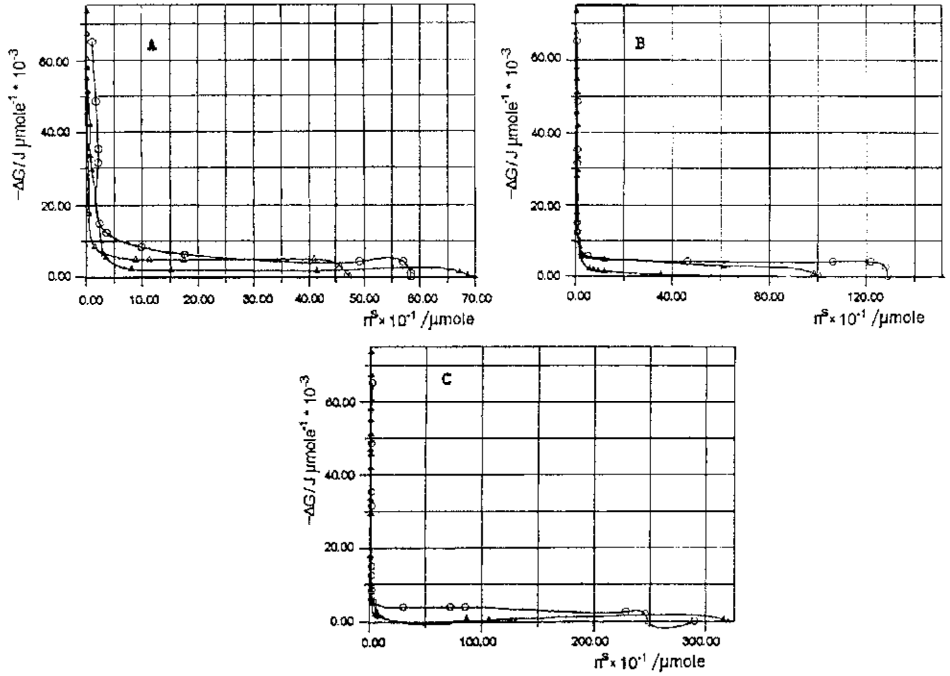

Fig. 5 Free molar enthalpy of adsorption of vapour of ▲ – benzene, △ – *n*-hexane and ○ – cyclohexene on different silica gels: A – Si40, B – Si60 and C – Si100

Figures 2–4 demonstrate that, up to the value of p/p_{s} corresponding to the initial point of the hysteresis loop, the numbers of μmoles of hydrocarbons ($n_{\mathrm{a}}^{\mathrm{s}}$) adsorbed on silica gel differ slightly irrespective of the porosity. However, significant differences between the amounts of vapour adsorbed if the hydrocarbons undergo capillary condensation ($n_{\mathrm{v}}^{\mathrm{s}}$) (Table 1). The values of $n_{\mathrm{v}}^{\mathrm{s}}$ were obtained from Eq. (2):

$$n_{\mathrm{v}}^{\mathrm{s}} = n^{\mathrm{s}} - n_{\mathrm{a}}^{\mathrm{s}} \tag{2}$$

where n_a^s is the number of μmoles of adsorbate in the adsorption layer, n^s is the total number of μmoles of vapour adsorbed at $p/p_s=1$, and n_v^s is the number of μmoles of adsorbate vapour undergoing capillary condensation after the adsorption layer has been formed.

Table 1 The quantities measured and calculation of the sorption of the adsorbates used on the examined silica gels

Silica gel	μmol m^{-2}	Benzene	Cyclohexene	*n*-Hexane
Si40	n^s	6.99	5.84	4.74
	n_v^s	6.67	5.60	4.59
	n_a^s	0.32	0.24	0.15
	n_v^s/n_a^s	20.80	23.30	30.60
Si60	n^s	15.17	12.87	10.08
	n_v^s	14.94	12.62	9.90
	n_a^s	0.23	0.25	0.18
	n_v^s/n_a^s	65.00	50.50	55.00
Si100	n^s	32.01	29.01	22.92
	n_v^s	31.80	28.83	22.80
	n_a^s	0.21	0.18	0.12
	n_v^s/n_a^s	151.00	160.20	190.00

Table 1 reveals that the amount of vapour condensed in the adsorbent pores is much greater than the amount of hydrocarbon adsorbed ($n_v^s>>n_a^s$). The quotient of n_v^s and n_a^s shows how many times the amount of condensed adsorbate vapour is greater than the amount adsorbed. The values of this quotient for a particular adsorbate are close for adsorbents with a given pore diameter. The results in Table 1 indicate that it is necessary to adjust the porosity when this procedure is planned for the storage of gases and vapours of volatile chemical compounds.

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