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A NEW METHOD FOR THE DETERMINATION OF SIMULTANEOUS ADSORPTION ISOTHERMS IN GAS-SOLID SYSTEMS BY MEANS OF GAS CHROMATOGRAPHY

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SUMMARY

Using a gas chromatograph, a system for the study of distribution equilibria in heterogeneous mixtures, of which one phase is a gas, was constructed. The method is described and evaluated for the determination of the simultaneous adsorption isotherms of two components in gas-solid systems. The precision and accuracy of the method are discussed. A brief outline of the theory underlying binary adsorption on solids is given. The simultaneous adsorption of a number of polar and non-polar adsorbates on hydrophilic and hydrophobic adsorbents has been determined.

INTRODUCTION

The measurement of mixed adsorption equilibria by gas chromatography (GC) has not been reported. The various dynamic GC methods¹ for the determination of distribution isotherms can in principle be adapted to systems in which simultaneous adsorption or dissolution of two (or more) components occurs. Applying these methods to such systems, the distribution of one component can be determined when the concentration of the others in the mobile phase is known. Accurate results cannot be expected, however, as the recorded signal curve does not originate from a single concentration profile if simultaneous adsorption occurs. In the minor disturbance method, a decrease in the resulting systematic error can be obtained. Other disadvantages of dynamic GC methods for the measurement of binary adsorption equilibria are interfering ghost peaks², caused by the sample injection, and the impossibility of using the full linear range of the detector for each component.

To overcome these disadvantages and difficulties, a new method was developed based on the principle of the GC equilibrium method¹. The compounds, of which the simultaneous adsorption is to be measured, are mixed with a carrier gas and led through a sample loop containing the adsorbent. After attainment of equilibrium, the contents of the sample loop are analyzed with a gas chromatograph. When, in addition to the sample loop containing adsorbent, a sample loop of known volume filled with the gas mixture only is used in precisely the same way as reference, all the parameters necessary for the calculation of the distribution data can be obtained.

The method is fast, precise, accurate and has an upper temperature limit, set by the material of the switching valves for the sample loops, of 350°.

Of the classical methods for measuring adsorption, only volumetric methods have been used to measure binary adsorption equilibria^{3,4}. These methods lack the speed, precision and temperature range of the new GC method.

THEORY

Distribution of a single component in a gas-solid system

From the point of view of statistical thermodynamics, the capacity ratio in adsorption and solution equilibria is determined by the ratio of the energy partition functions of the distributed component in the various phases:

$$\kappa_i = \frac{N_i^\sigma}{N_i^\alpha} = \frac{q_i^\sigma}{q_i^\alpha} = \frac{\sum e^{-\varepsilon_i^\sigma/kT}}{\sum e^{-\varepsilon_i^\alpha/kT}} \quad (1)$$

where

- κ_i = capacity ratio (mass partition ratio) of component i between the solid surface layer σ and the gas phase α
- N_i^σ and N_i^α = total number of molecules of component i in the solid surface layer σ and the gas phase α , respectively
- q_i^σ and q_i^α = energy partition functions of component i in the phases σ and α , respectively
- ε_i^σ and ε_i^α = total energy state of a molecule of component i
- T = thermodynamic temperature
- k = Boltzmann constant.

When a molecule is adsorbed, losses and changes in degrees of translation, rotation and vibration may occur. Also, allowance must be made for multi-layer formation, interaction of the adsorbed molecules, lattice distortion of the adsorbed layer, surface heterogeneity and capillary condensation. Taking these effects into account, various complex equations can be derived⁵⁻⁷, usually fitting only some parts of the experimental distribution isotherms.

In the simplest case of adsorption, corresponding to the assumption of a mobile monomolecular adsorbed layer, one degree of translation is replaced by one of vibration perpendicular to the surface of the adsorbent.

Applying eqn. 1 results in:

$$\kappa_i = \frac{q_z^\sigma \cdot \int_0^A (e^{-\omega_i^\sigma/kT} - 1) dA}{\sqrt{2\pi m_i kT} \cdot (V_\alpha + B_i^\alpha)} \quad (2)$$

where

- q_z^σ = energy partition function corresponding to the vibration of the adsorbed molecule perpendicular to the adsorbent surface
- ω_i^σ = extra molecular free enthalpy of component i in the adsorbed surface layer σ on the solid

- A = surface area of the solid
 m_i = molecular mass of component i
 V_α = volume of the gas phase α
 B_i^α = second virial coefficient of component i in the gas phase α .

In the case of an ideal gas, an energetically homogeneous surface and no mutual interaction of the adsorbed molecules, eqn. 2 can be written as:

$$\kappa_i = K_{i0} \cdot \frac{A}{V_\alpha} \quad (3)$$

where K_{i0} is a constant for a given phase system and temperature.

If the energy of adsorption is high ($-\omega_i^\sigma \gg kT$), a mobile adsorbed layer cannot exist and localized (site) adsorption can be assumed to occur. This makes it necessary to account for a configurational degeneracy in the partition function Q for the adsorbed state:

$$Q = \frac{N!}{N_i!(N - N_i)!} \cdot q^N \quad (4)$$

where

- N = total number of sites on surface
 N_i = number of adsorbed molecules (one molecule per site)
 q = energy partition function for an adsorbed molecule.

Using eqns. 1 and 4 and assuming monolayer adsorption on an energetically homogeneous surface and no mutual interaction of the adsorbed molecules results in:

$$\kappa_i = \frac{C_0}{C_i + N_i^\alpha} \quad (5)$$

where:

- C_0 = a constant proportional to the number of adsorption sites on the surface of the adsorbent
 C_i = a function of the component i and constant for a given phase system and temperature.

Distribution of a binary mixture in a gas-solid system

The simultaneous distribution of two components in gas-solid systems has been described theoretically^{8,9} and calculated from the individual adsorption isotherms of the pure components^{10,11}, always on the basis of simplified conditions.

When both components are adsorbed in a mobile monomolecular layer and mutual interaction is neglected, the isotherms for binary adsorption can be described by eqn. 3 for the individual components. For localized adsorption, eqns. 1 and 4 can be applied to binary adsorption and the following equations are obtained for components i and j :

$$\kappa_i = \frac{C_0 C_j}{C_i C_j + C_j N_i^\alpha + C_i N_j^\alpha} \quad (6a)$$

$$\kappa_j = \frac{C_0 C_i}{C_i C_j + C_j N_i^\alpha + C_i N_j^\alpha} \quad (6b)$$

According to eqn. 5, the capacity ratios of the pure components i and j are given by:

$$\kappa_i = \frac{C_0}{C_i + N_i^\alpha} \quad \text{and} \quad \kappa_j = \frac{C_0}{C_j + N_j^\alpha}$$

Eqns. 6a and 6b can be rearranged to give:

$$N_i^\sigma = - \frac{N_i^\alpha}{C_i + N_i^\alpha} \cdot N_j^\sigma + \frac{C_0 N_i^\alpha}{C_i + N_i^\alpha} \quad (7a)$$

$$N_j^\sigma = - \frac{N_j^\alpha}{C_j + N_j^\alpha} \cdot N_i^\sigma + \frac{C_0 N_j^\alpha}{C_j + N_j^\alpha} \quad (7b)$$

which are linear functions for constant N_i^α or N_j^α , the number of molecules of component i or j in the gas phase α . The assumption of monomolecular site adsorption and no mutual interaction of the molecules thus predicts a linear relationship between N_i^σ and N_j^σ .

EXPERIMENTAL

Apparatus

The arrangement shown in Fig. 1 was used to determine the simultaneous sorption of the components of a gas mixture.

A mixture (Air Liquide) of 99 % helium and 1 % nitrogen (by volume) is used as carrier gas for the components of which the sorption is to be measured. The carrier gas mixture is taken from a pressure cylinder (A) over a reducing valve and is adjusted to a constant pressure by a pressure control valve (P_1 , Fairchild Hiller Kendall 30) and purified by an adsorption unit (G_1), after which the gas stream is split into two. The flow-rate of each gas stream can be adjusted by mass flow controllers (F_1 and F_2 , Brooks 8743) and capillary restrictors (R_1 and R_2). The pressure control valve, gas purifier, mass flow controllers and restrictors are thermostatted in an air-bath (T_1 , Becker 1452 P) at 40° to within $\pm 0.2^\circ$. The two gas streams are led to evaporation columns (E_i and E_j) in which they are saturated with the vapours of components i and j , of which the sorption is to be studied. The resulting gas streams are mixed and led to a sampling valve (S_1). The evaporation columns consist of copper tubes, 500 \times 4 mm, packed with a solid support (Chromosorb W, Johns-Manville) which is coated to a level of 40–50 % by weight with the components i and j . The vapour pressure of each adsorbate is controlled by the temperature of the corresponding evaporation column, which is contained in a liquid-bath thermostat (T_2 and T_3 , Haake F). The temperature range used for adjusting the vapour pressures is from -70° to ambient, and for this purpose methanol is used as the bath liquid. The bath liquid is circulated from each thermostat through separate heat exchangers contained in a Dewar flask,

which is cooled with liquid nitrogen to a temperature of about 20° below the lowest temperature in the thermostats. Cryogenic equipment (Cryoson Alpha TRL-1B and CT-25R) is used to control the temperature in the Dewar flask. Temperature constancy along the evaporation columns in the thermostats was found to be better than 1° .

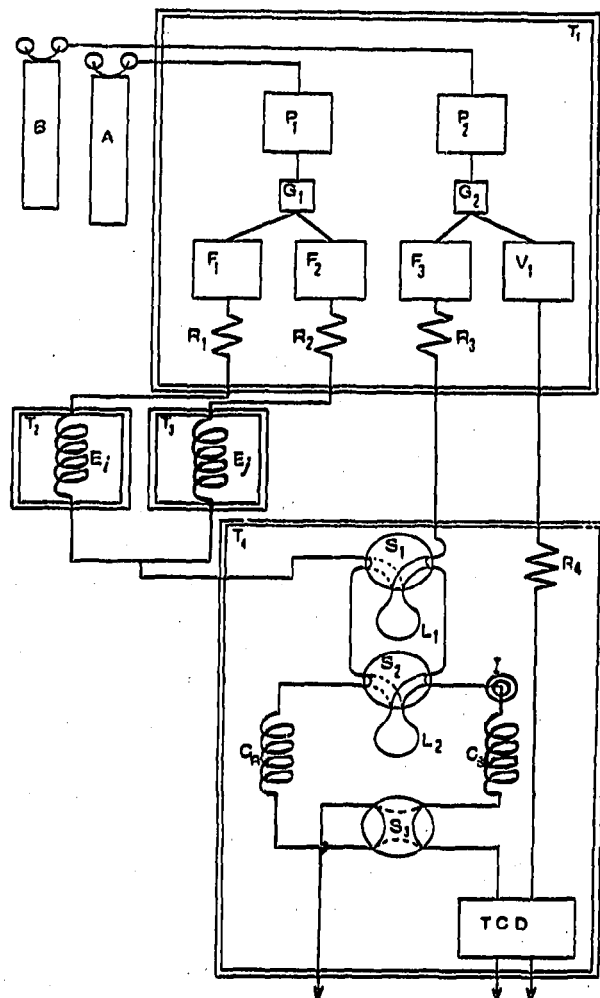


Fig. 1. Block diagram of the apparatus for the determination of adsorption data. A and B, gas cylinders; P_1 and P_2 , pressure controllers; G_1 and G_2 , gas purifiers; F_1 , F_2 and F_3 , mass flow controllers; V_1 , needle valve; R_1 , R_2 , R_3 and R_4 , capillary restrictors; T_1 , T_2 , T_3 and T_4 , thermostats; E_1 and E_2 , evaporation columns; S_1 , S_2 and S_3 , switching valves; L_1 and L_2 , sample tubes; I, injection port; C_R , inert column; C_S , chromatographic separation column; TCD, thermal conductivity detector.

Pure helium (Air Liquide) is used as the carrier gas in the chromatographic separation column (C_S) and is obtained from a pressure cylinder (B). The gas is led through a reducing valve, a pressure controller (P_2 , Fairchild Hiller Kendall 30) and gas purifier (G_2) after which the gas stream is split into two. One part of the gas stream is controlled by a mass flow controller (F_3 , Brooks 8743) and capillary restrictor (R_3) and is led to the second inlet of the sampling valve (S_1). The other part of the gas stream is used as the reference flow for the detector and is adjusted by the use of a needle valve (V_1 , Brooks 8501) and capillary restrictor (R_4). The

control elements (P_2 , F_3 , V_1 , R_3) and the gas purifier (G_2) are thermostatted in the same air-bath (T_1). The restrictor (R_4) in the detector reference flow path is contained in the chromatographic air-bath (T_4). The gas purifiers (G_1 , G_2) consist of PTFE tubes of 4-mm I.D. and 150-mm length filled with activated molecular sieve (Linde 4A). At the outlet, metal filters (Brooks 1390) are installed. The capillary restrictors (R_1 , R_2 , R_3 , R_4) consist of copper capillary tubes of 0.1-mm I.D. and 5-m length.

By switching the sampling valve (S_1 , Valco VSV-6HT) either the carrier gas mixture ($\text{He} + 1\% \text{N}_2$) containing the vapour of components i and j from the evaporation columns, or pure helium is led through a sample tube (L_1), packed with the adsorbent to be studied. In the first case, the adsorbate compounds i and j are adsorbed and in the second case they are desorbed. A second sampling valve (S_2 , Valco VSV-6HT) is connected in series with the first (S_1), so that, depending on its switching position, the corresponding sample tube (L_2) is flushed with pure helium or with the helium-nitrogen-adsorbates mixture. The second sample tube (L_2) contains no adsorbent and has a precisely known volume, which, including the volume of the valve connections, is 4.05 cm³. The volume of the sample tube containing adsorbent (L_1) has to be chosen for optimum accuracy and precision. In the case of weak adsorption, a tube of 10-cm length and 4-mm I.D., and in the case of strong adsorption, a tube of 5-cm length and 1-mm I.D., are used.

After having passed both sampling valves, the gas mixture containing the adsorbate compounds is led through an inert column (C_R), acting as a flow restrictor, to a switching valve (S_3 , Valco CV-4-HT). The stream of pure helium is led from the sampling valves through an injection port (I) and a chromatographic separation column (C_S) to the same switching valve (S_3). Depending on the position of the switching valve, either the effluent of the restrictor column or the chromatographic column is fed to a thermal conductivity detector (TCD) or to waste. The chromatographic column consists of a copper tube of 1-m length and 4-mm I.D. filled with a chromatographic packing suitable for the required separation. The restrictor column has the same dimensions and is filled with an inert packing material of the same particle size as is used for the chromatographic column. The sampling valves and sample tubes, injection port, columns and switching valve are held at the same temperature to within $\pm 0.2^\circ$ by a thermostatted air-bath (T_4 , Becker 1452 P).

A TCD of small volume and low noise (Servomex, cell MK 158/GC 197, Catharometer control unit 197) is used to measure the concentration of the adsorbate compounds in the effluent of the chromatographic column. It is also used to monitor the effluent of the restrictor column in order to check the attainment of equilibrium in the sample tube filled with adsorbent. The TCD cell is placed in the chromatographic air-bath (T_4). The detector signal is processed by a digital integrator (Infotronics, CRS 104) and displayed on a potentiometric recorder (Siemens Kompensograph III).

Simultaneous adsorption data for compounds i and j on a solid adsorbent are derived from chromatographic measurement of the adsorbate contents of the two sample tubes, one containing the adsorbent in equilibrium with the gas mixture and the other containing the gas mixture only. An example of the chromatograms resulting from injecting the contents of both sample tubes, one after the other, into the chromatographic column is shown in Fig. 2. The concentration of component i in the gas phase in terms of molarity is calculated from the area A_{i2} of the

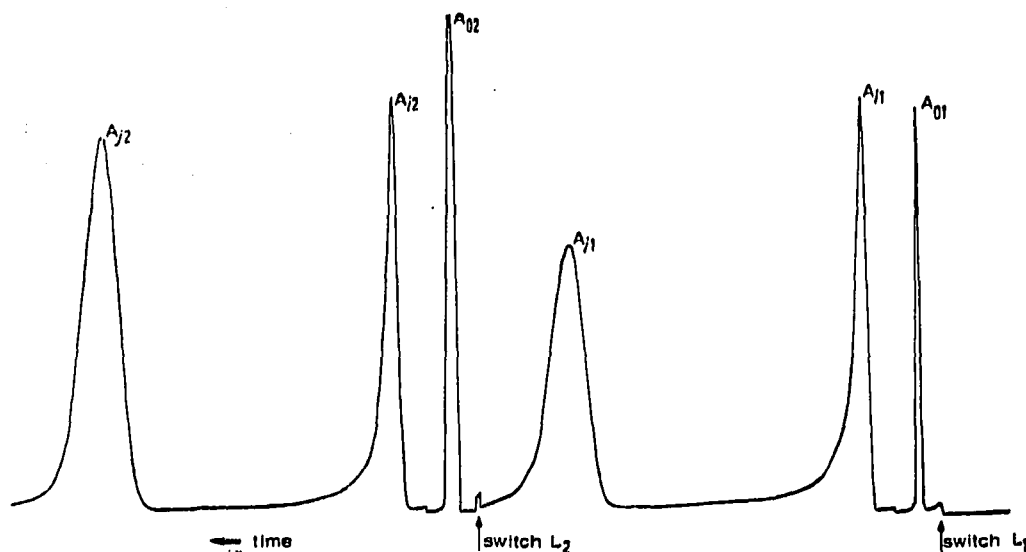


Fig. 2. Chromatograms resulting from the successive injection of the contents of the sample tubes L_1 and L_2 into the chromatographic column C_S (Fig. 1). Sample: water (i) - ethanol (j). Adsorbent: Chromosorb W NAW, 120° . Chromatographic column: Porapak Q, 120° ; attenuation: nitrogen (A_{01} , A_{02}) $\times 20$, other peaks $\times 4$.

corresponding peak in the chromatogram of the contents of the sample tube without adsorbent and of known volume V_2 :

$$c_i^g = \frac{A_{i2}}{S_{Qi}V_2} \quad (8)$$

where

S_{Qi} = sensitivity of the detector-integrator system with respect to the amount Q of component i .

The concentration in the gas phase can also be described by the partial pressure instead of the molarity. By applying the ideal gas law, the partial pressure in the sample tubes can be calculated from the molarity obtained by eqn. 8.

The concentration c_i^σ , defined as the amount of component i in the surface layer of the adsorbent related to the mass m_s of the adsorbent, is calculated from:

$$c_i^\sigma = \frac{A_{i1} - \frac{A_{01}}{A_{02}} \cdot A_{i2}}{S_{Qi} \cdot m_s} \quad (9)$$

where

A_{i1} = peak area resulting from the amount of component i in the sample tube containing the adsorbent

A_{01} , A_{02} = peak areas resulting from the inert tracer (nitrogen) in the two sample tubes, containing adsorbent and no adsorbent, respectively.

The use of an inert tracer makes it possible to calculate the peak area corresponding to the amount of component i in the gas phase of the sample tube containing the adsorbent ($(A_{01}/A_{02}) \cdot A_{i2}$).

The sensitivity of the detector-integrator system can be determined by injecting known amounts of the adsorbates through the injection port (I) of the chromatographic column with a precision syringe (Hamilton). If the vapour pressure p_i^0 at the temperature of the evaporation column is known, the calibration can also be carried out by connecting each evaporation column separately to the switching valves (S_1, S_2). In both cases the sensitivity is calculated from the resulting peak area:

$$S_{Q_i} = \frac{A_i}{Q_i} = \frac{A_{i2}}{p_i^0 \cdot V_2} \cdot RT \quad (10)$$

where

R = gas constant

T = temperature of the sample tube L_2 .

Flow-rates through the restrictor column and chromatographic column are balanced by means of flow controllers (F_1, F_2). The set points of the flow controllers are found by measuring the flow-rate at the detector outlet by a flow meter (Brooks Vol-U-Meter 1052) when each column outlet is connected to the detector separately through the switching valve (S_3).

As long as nitrogen is not adsorbed significantly, the density ρ_s of a solid can be determined from the areas of the nitrogen peaks A_{01} and A'_{01} , which are obtained from the same sample tube (L_1) containing a known mass of solid and no solid, respectively:

$$\rho_s = \frac{A_{02}}{A'_{01} - A_{01}} \cdot \frac{m_s}{V_2} \quad (11)$$

The density of solids was also determined with a gas pycnometer (Schildknecht, Volumeter M 712).

Specific surface areas of the adsorbents were determined according to the BET method with a volumetric instrument (Ströhlein, Areameter).

Chemicals

Depending on the type of sample, a polydivinylbenzene-type adsorbent (Porapak Q, 0.1-0.2 mm, Waters) or squalane (Merck) coated to 5% by weight on a silanized diatomaceous earth support (Chromosorb G, 0.1-0.2 mm, Johns-Manville) was used as packing material in the chromatographic column.

The following adsorbents were included in the study: glass beads, 0.1-0.2 mm, <0.3 m²/g (Corning); refined diatomaceous earth, 0.1-0.2 mm, 1.1 m²/g (Chromosorb W NAW, Johns-Manville); silica, 0.1-0.2 mm, 460 m²/g (Merck) and porous polydivinylbenzene-type adsorbent, 0.1-0.2 mm, 630 m²/g (Porapak Q, Waters).

The adsorption of the following compounds was investigated: pentane, hexane, benzene, acetone, ethanol, methanol and water. All these compounds were of analytical grade (Merck).

RESULTS AND DISCUSSION

Detector characteristics

The linear dynamic range of the micro-TCD was tested with pentane for a helium flow of 15 ml/min at a temperature of 100° and using a bridge potential of 775 mV. The standard deviation of the noise of the baseline was found to be 3 μ V (Fig. 3). The response was linear within 1% up to 200 mV. The linear dynamic

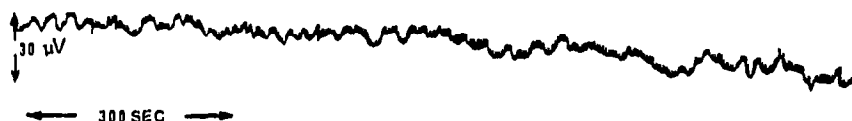


Fig. 3. Noise pattern of the micro-catharometer.

range therefore amounts to almost 10^5 . In Fig. 4, the results are given in the form of a logarithmic plot of the detector signal *versus* the inverse of the absolute temperature at which the pentane vapour is generated. By calibrating the ordinate in pressure units by the use of data from the literature¹², the sensitivity of the detector with respect to the partial pressure for pentane was found to be 2.2 V/bar. With the value of the sensitivity, it can be calculated that the standard deviation of the baseline noise is equivalent to a partial pressure of about 1 μ bar.

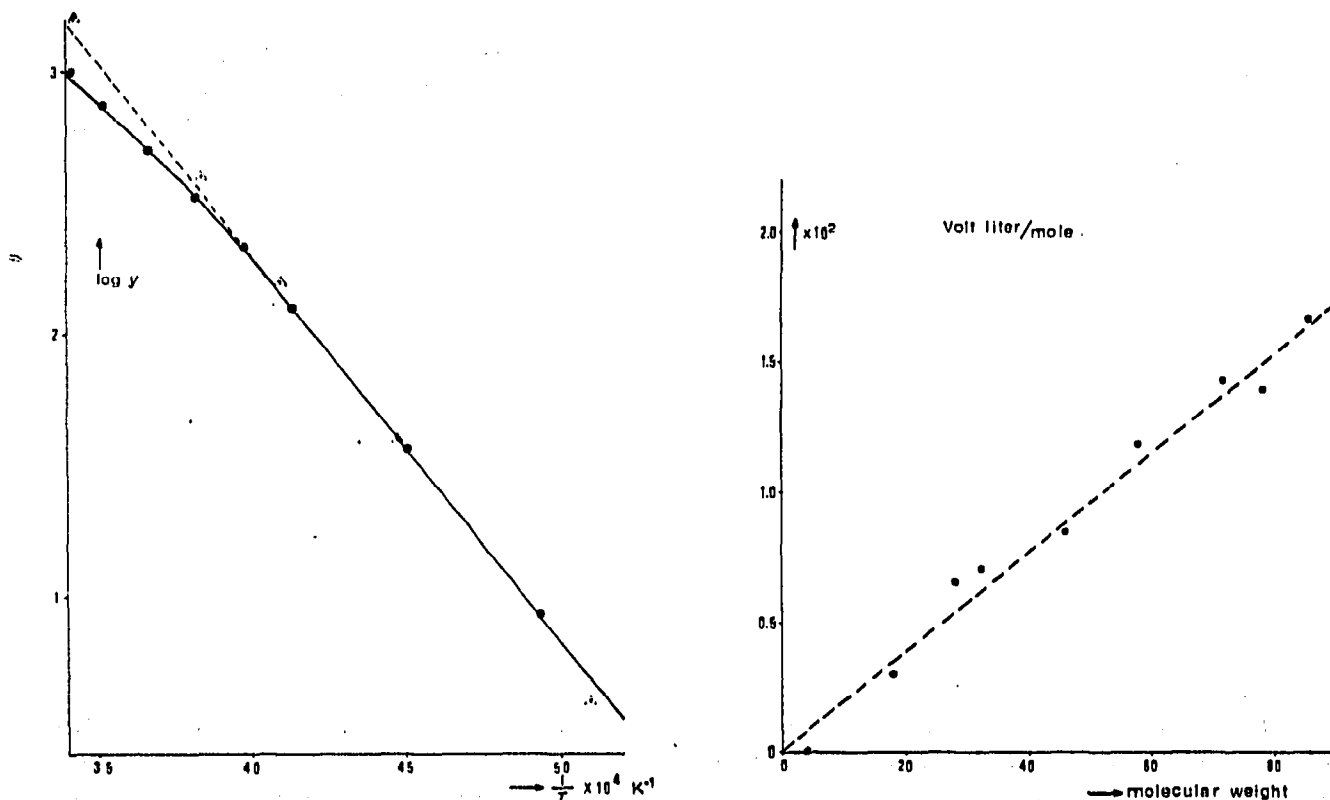


Fig. 4. Graphical representation of the linear dynamic range of the micro-catharometer. y = Detector output signal in mV; T = absolute temperature of the evaporation column; \bullet = experimental data; Δ = data from the literature¹².

Fig. 5. Plot of the sensitivity (volt·litre/mole) of the micro-catharometer for the compounds listed in Table I *versus* their molecular weights.

In Fig. 5, a plot is given of the detector sensitivities, which were determined for the various compounds used, *versus* their molecular weights. The molar response of these compounds relative to benzene was calculated. In Table I the results are compared with data from the literature¹³ and satisfactory agreement is found.

TABLE I

COMPILATION OF RELATIVE MOLAR RESPONSE DATA FOR THE TCD

Component	Experimental	Literature ^{13,14}
Helium	0	0
Water	23	21-33
Nitrogen	48	42
Methanol	51	55
Ethanol	70	72
Acetone	85	86
Benzene	100	100
Pentane	103	105
Hexane	120	123

Densities of porous solids

The densities of glass beads, Chromosorb W, silica and Porapak Q were determined by the GC method according to eqn. 11 and by the gas pycnometric method. In Table II the results are given for glass beads and for Chromosorb W only, as the densities of Porapak and silica could not be determined accurately owing to the significant adsorption of nitrogen.

TABLE II

DENSITY OF ADSORBENTS MEASURED BY GAS CHROMATOGRAPHIC AND GAS PYCNOMETRIC METHODS

The results are given with a confidence limit of $\pm 3\sigma$; average values of five measurements were taken.

Adsorbent	Density (g/cm ³)	
	GC method	Pycnometric method
Chromosorb W	2.32 \pm 0.2	2.64 \pm 0.04
Glass beads	2.91 \pm 0.05	2.95 \pm 0.04

Binary gas-solid adsorption data

The simultaneous adsorption equilibrium of a binary gas mixture on a solid surface can be described by three independent thermodynamic variables. In this paper, the temperature T is chosen as one of these variables and is taken as being constant. Depending on the choice of the other independent variables, two types of isotherms are used for the description of adsorption equilibria in this paper:

$$c_i^{\sigma} = f(p_i)_{T,p_j} \quad \text{and} \quad c_i^{\sigma} = f(c_j^{\sigma})_{T,p_i} \quad (12)$$

The concentration in the gas phase is expressed by the partial pressure p_i (mm of Hg at 0°). Average values of three measurements are given for the adsorption data.

Precision and accuracy. Taking m_s and V_{g2} as constant, it can be calculated from eqns. 8 and 9 that the relative standard deviations in determining c_i^g and c_i^s are given by:

$$\left(\frac{\sigma_c}{c_i^g}\right)^2 = \left(\frac{\sigma_{A_i}}{A_i}\right)^2 + \left(\frac{\sigma_{S_{Q_i}}}{S_{Q_i}}\right)^2 \quad (13)$$

$$\left(\frac{\sigma_c}{c_i^s}\right)^2 = \left(\frac{\sigma_{A_i}}{A_i}\right)^2 \cdot \left[1 + \frac{2(1 + \kappa_i)}{\kappa_i^2}\right] + \frac{2}{\kappa_i^2} \cdot \frac{\sigma_{A_0}}{A_0} + \frac{1}{\kappa_i^2} \left(\frac{\sigma_{S_{Q_i}}}{S_{Q_i}}\right)^2 \quad (14)$$

where

$$\kappa_i = \frac{A_{i1} - \left(\frac{A_{01}}{A_{02}} \cdot A_{i2}\right)}{\frac{A_{01}}{A_{02}} \cdot A_{i2}}$$

σ_c/c_i^g and σ_c/c_i^s = relative standard deviations of the adsorbate concentrations in the gas phase and the surface layer, respectively

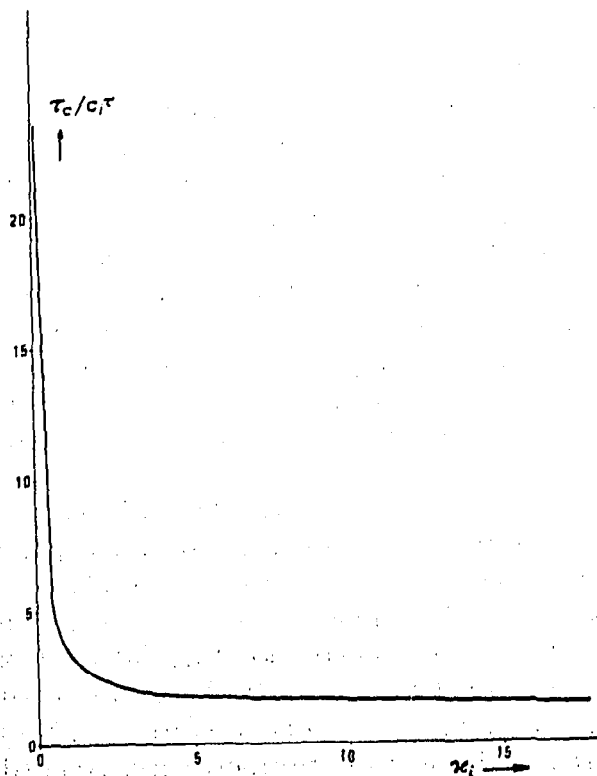


Fig. 6. Plot of the relative standard deviation σ_c/c_i^s (%) in the surface layer concentration as a function of the capacity ratio κ_i of component i .

σ_{A_i}/A_i	= relative standard deviation of the peak areas for the adsorbates
σ_{A_0}/A_0	= relative standard deviation of the peak areas for nitrogen
$\sigma_{S_{Q_i}}/S_{Q_i}$	= relative standard deviation of the sensitivity of the detector-integrator system.

σ_{A_i}/A_i and σ_{A_0}/A_0 were found to be 1.5 % and 0.3 %, respectively. Substituting these values in eqn. 14, σ_c/c_i^σ is obtained as a function of κ_i if the fluctuation of the sensitivity is neglected. The result is plotted in Fig. 6, where it can be seen how the statistical error decreases with the capacity ratio. The contribution of the chromatographic procedure to the total precision (1.5 %) of the adsorbate determination is indicated by the precision of the nitrogen determination (0.3 %). The difference in the standard deviation of the peak area for the adsorbates and nitrogen can be ascribed to the fluctuation of vapour pressure of the adsorbates, which thus determines the total precision of the peak area for the adsorbates. The magnitude of the effect of the temperature fluctuations in the thermostats for the evaporation columns on the pressure of the vapour generated can be estimated from:

$$\frac{d \ln p_i^0}{dT} = \frac{1}{p_i^0} \cdot \frac{dp_i^0}{dT} = - \frac{23T_b}{RT^2} \quad (15)$$

where

p_i^0 = vapour pressure generated at temperature T

T_b = boiling point

23 = Trouton constant ($\text{cal} \cdot ^\circ\text{K}^{-1} \cdot \text{mol}^{-1}$).

For the adsorbates used, this gives a relative vapour pressure change of 4–8 % per degree change in temperature. This corresponds to a standard deviation in the temperature of about 0.2° for a standard deviation in the pressure of 1.5 %.

The accuracy of the adsorption data depends on the accuracy of the sensitivity S_{Q_i} , which in turn is affected mainly by the accuracy of the temperature read out from the thermostats. The accuracy was estimated at 3 %. Another factor affecting the accuracy is the extent to which nitrogen is adsorbed on the solid. The total peak area A_{01} corresponds to the amount of nitrogen present in the gas phase and on the solid surface. If nitrogen is adsorbed significantly, eqn. 9 has to be corrected by replacing the peak area A_{01} by the part of it which corresponds to the nitrogen contents of the gas phase only. This can be calculated from eqn. 11 if the density of the solid is known.

Adsorption of binary gas mixtures on hydrophilic solid surfaces. The adsorbates, adsorbents and temperatures used in the measurement of simultaneous adsorption equilibria of binary gas mixtures on hydrophilic surfaces are given in Table III.

In Fig. 7 (a–d), some results in the capacity ratio range of 0.5 to 5 are given. The precision according to Fig. 6 is 2–5 %. In Fig. 8, the corresponding adsorption functions are given in a plot of the surface layer concentration (c_i^σ) of the one component (i) versus the surface layer concentration (c_j^σ) of the other component (j) at constant pressure of the (isobaric) component i and constant temperature. According to eqn. 7, straight lines with a slope (dN_i^σ/dN_j^σ) between 0 and -1 can be expected for monolayer adsorption with no nearest neighbour interaction on an

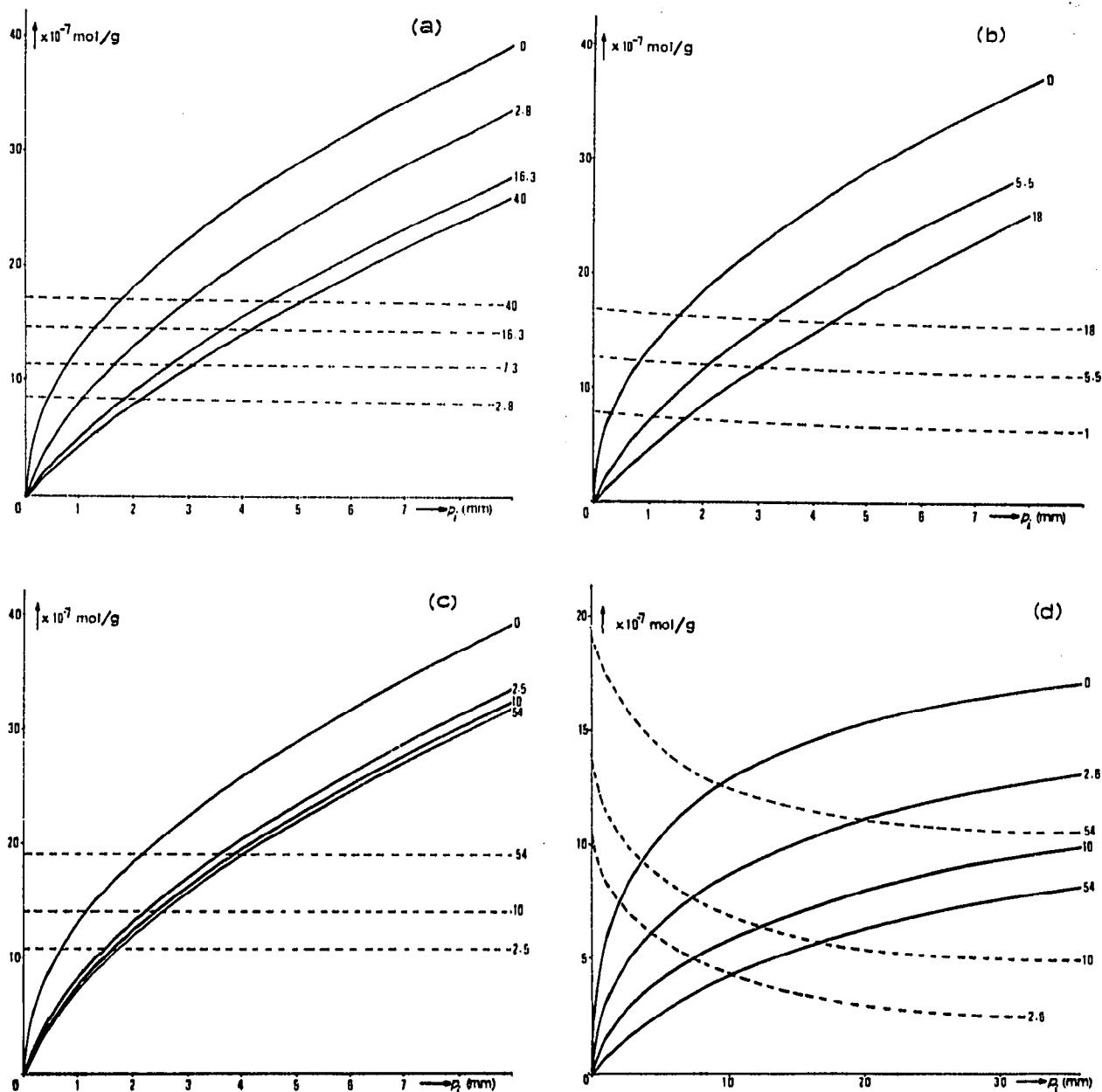


Fig. 7. Simultaneous adsorption of binary mixtures on Chromosorb W NAW at 120° . The surface layer concentration c_i^{σ} (mol/g) of one component (i) is plotted as a function of its partial pressure p_i (mm) at constant partial pressure p_j (mm), indicated by the indices, of the other component.

i	j
(a) (—) water	methanol
(----) methanol	water
(b) (—) water	ethanol
(----) ethanol	water
(c) (—) water	acetone
(----) acetone	water
(d) (—) methanol	acetone
(----) acetone	methanol

TABLE III

SYSTEMS IN WHICH THE SIMULTANEOUS ADSORPTION ON HYDROPHILIC SURFACES WAS MEASURED

Adsorbates		Temperature ($^{\circ}$ C)		
		Adsorbents		
		Glass beads	Chromosorb W NAW	Silica
Water	Methanol	—	120	—
Water	Ethanol	120	120	—
Water	Acetone	—	120	—
Water	Benzene	—	100	100
Water	Hexane	—	100	100
Methanol	Acetone	120	120	—
Acetone	Benzene	100	100	100
Acetone	Hexane	—	100	100
Benzene	Hexane	—	100	100
Hexane	Pentane	—	100	60, 100

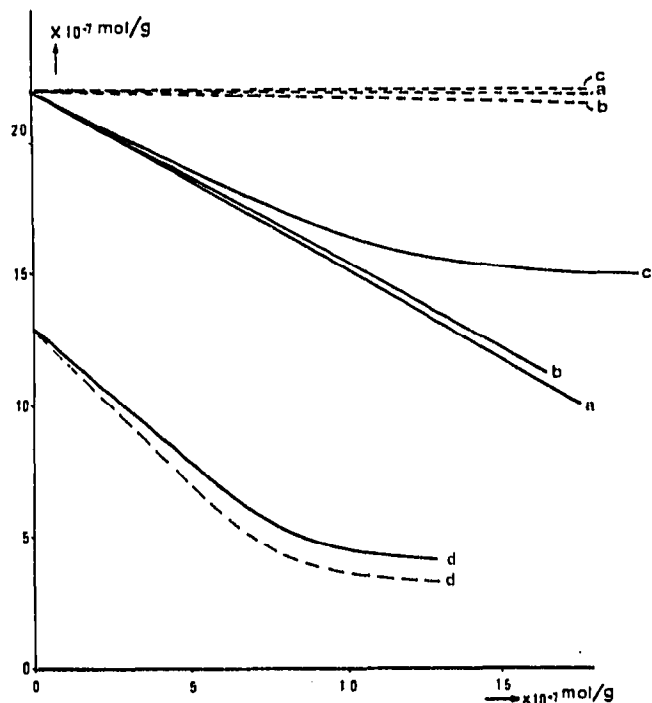
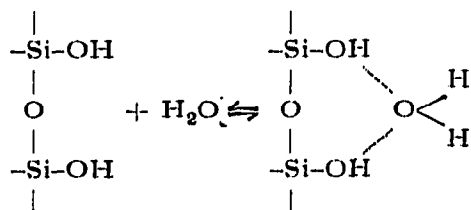


Fig. 8. Simultaneous adsorption of binary mixtures on Chromosorb W NAW at 120° . The surface layer concentration $c_{i\sigma}$ (mol/g) of one component (i) is plotted as a function of the surface layer concentration $c_{j\sigma}$ (mol/g) of the second component (j) at constant partial pressure p_i of the first component.

i	j	p_i (mm)
(a) (—) water	methanol	2.7
(- - -) methanol	water	120
(b) (—) water	ethanol	2.7
(- - -) ethanol	water	60
(c) (—) water	acetone	2.7
(- - -) acetone	water	140
(d) (—) methanol	acetone	10
(- - -) acetone	methanol	7

energetically homogeneous surface. In Fig. 8, it can be seen that at a low surface coverage of the non-isobaric compound (j) a linear relation is indeed observed.

The differences in the curves for the various compounds can partly be explained by considering the chemical nature of Chromosorb W. Its surface contains hydroxyl groups on which specific adsorption takes place¹⁵. Single (Si-OH) and *geminal* (Si< $\begin{smallmatrix} \text{HO} \\ \text{HO} \end{smallmatrix}$) hydroxyl groups can be distinguished on the surface. The single hydroxyl (silanol) groups can be positioned *vicinal* or can be isolated. Depending on the degree of dehydration, siloxane (Si-O-Si) groups may also be present. Water adsorption appears to be strongest¹⁶ on siloxane sites, where it is chemisorbed, and on *geminal* and *vicinal* hydroxyl sites. From Figs. 7 and 8, it can be seen that the adsorption of methanol, ethanol and acetone is little influenced by the presence of water at low surface coverage. These results are in agreement with other results reported in the literature¹⁷. On the other hand, the adsorption of water is influenced significantly by the presence of methanol, ethanol or acetone. This can be explained by the fact that new hydroxyl groups are formed where water is adsorbed on the surface by hydrogen bonding, which results in site continuance, *e.g.*:



Methanol, ethanol and acetone appear to be adsorbed with almost equal strength on the new hydroxyl sites as on the old ones. The water molecules, however, have to compete for the hydroxyl sites with methanol, ethanol or acetone. The same competition occurs when methanol and acetone are simultaneously adsorbed (Figs. 7d and 8d), where it appears that acetone is adsorbed more strongly than methanol. This results in a decreasing influence of both adsorbed compounds on each other at increasing surface coverage of the non-isobaric compound, as shown in Fig. 8d.

The measurements of the binary adsorption of benzene, hexane and pentane on Chromosorb W were not so precise, owing to the low capacity ratios of these compounds, ranging from about 0.5 to 0.005, respectively (corresponding to a precision of 5–100%). A possibility for achieving better precision would be to increase the capacity ratios by increasing the packing density of the adsorbent. An increase in packing density, however, causes an increase in pressure drop across the sample loop, which may affect the accuracy¹.

The results for the adsorption of the binary gas mixtures studied on Chromosorb W were almost identical with the results obtained on glass beads and silica if the surface concentration (amount of a component adsorbed per unit surface area) was considered. On silica, components such as benzene, hexane and pentane have capacity ratios that are two orders of magnitude greater than on Chromosorb W and they can therefore be studied with a much better precision. On silica, however, nitrogen was found to be measurably adsorbed and an adsorption coefficient of 0.9 cm³/g was calculated using a density value of 2.3 g/cm³ for silica. The adsorption

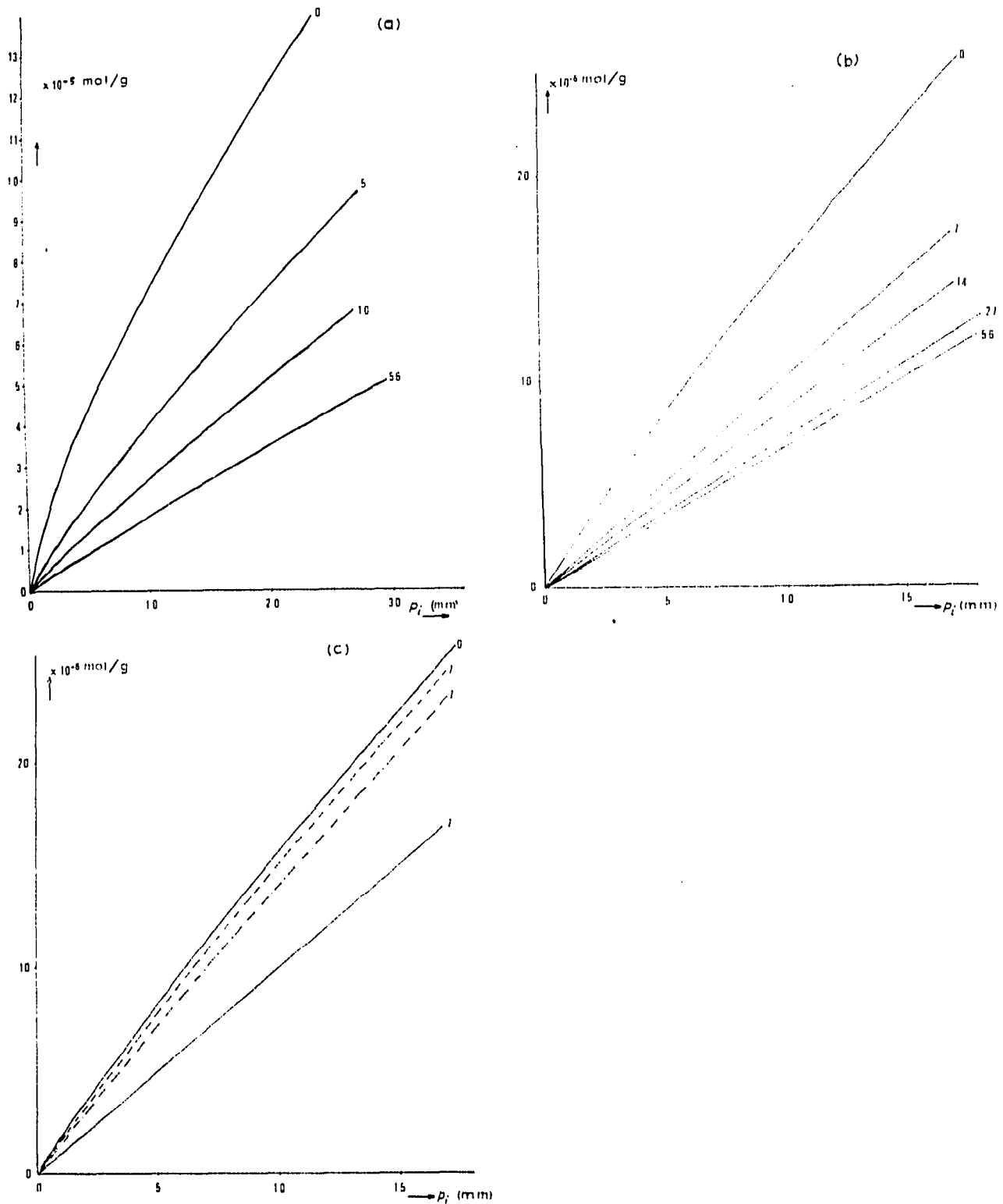


Fig. 9. Simultaneous adsorption of binary mixtures on silica at 100°. Plot as in Fig. 7.

	<i>i</i>	<i>j</i>
(a)	benzene	acetone
(b)	hexane	acetone
(c) (---)	hexane	water
(-·-·-)	hexane	benzene
(—)	hexane	acetone

of nitrogen was taken into account in the calculation of the adsorption data according to eqn. 9. Adsorption isotherms for benzene on silica at various partial pressures of acetone are given in Fig. 9a. It can be seen that acetone competes effectively with benzene for the adsorption sites. Water appeared to have virtually no influence on the adsorption of benzene (site continuance), and neither did hexane (weak adsorption). The effect of the simultaneous adsorption of hexane and acetone on silica is shown in Fig. 9b. It can be seen from Figs. 9a and b that acetone reduces the adsorption of benzene more than the adsorption of hexane. Adsorption isotherms of hexane on silica at constant partial pressures of acetone, benzene or water are shown in Fig. 9c. Water appeared to have the least influence and acetone the greatest. The dependence of binary adsorption on temperature is demonstrated for pentane and hexane on silica gel at 60° and 100° in Fig. 10.

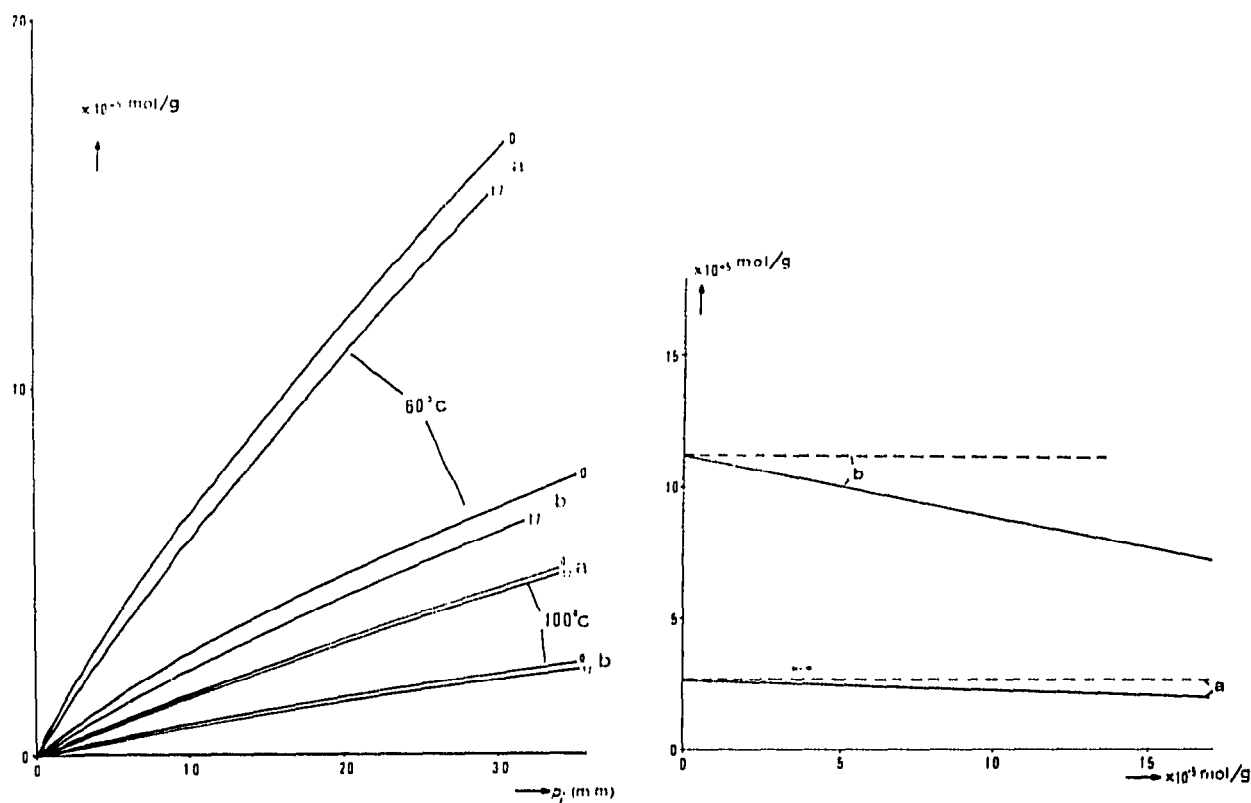


Fig. 10. Simultaneous adsorption of pentane-hexane mixtures on silica at 60° and 100°. Plot as in Fig. 7.

	<i>i</i>	<i>j</i>
(a)	hexane	pentane
(b)	pentane	hexane

Fig. 11. Simultaneous adsorption of binary mixtures on silica at 100°. Plot as in Fig. 8.

	<i>i</i>	<i>j</i>	p_i (mm)
(a) (— — —)	hexane	benzene	2
	hexane	acetone	2
(- - - -)	hexane	water	2
(b) (— — —)	benzene	acetone	16
	benzene	water	16

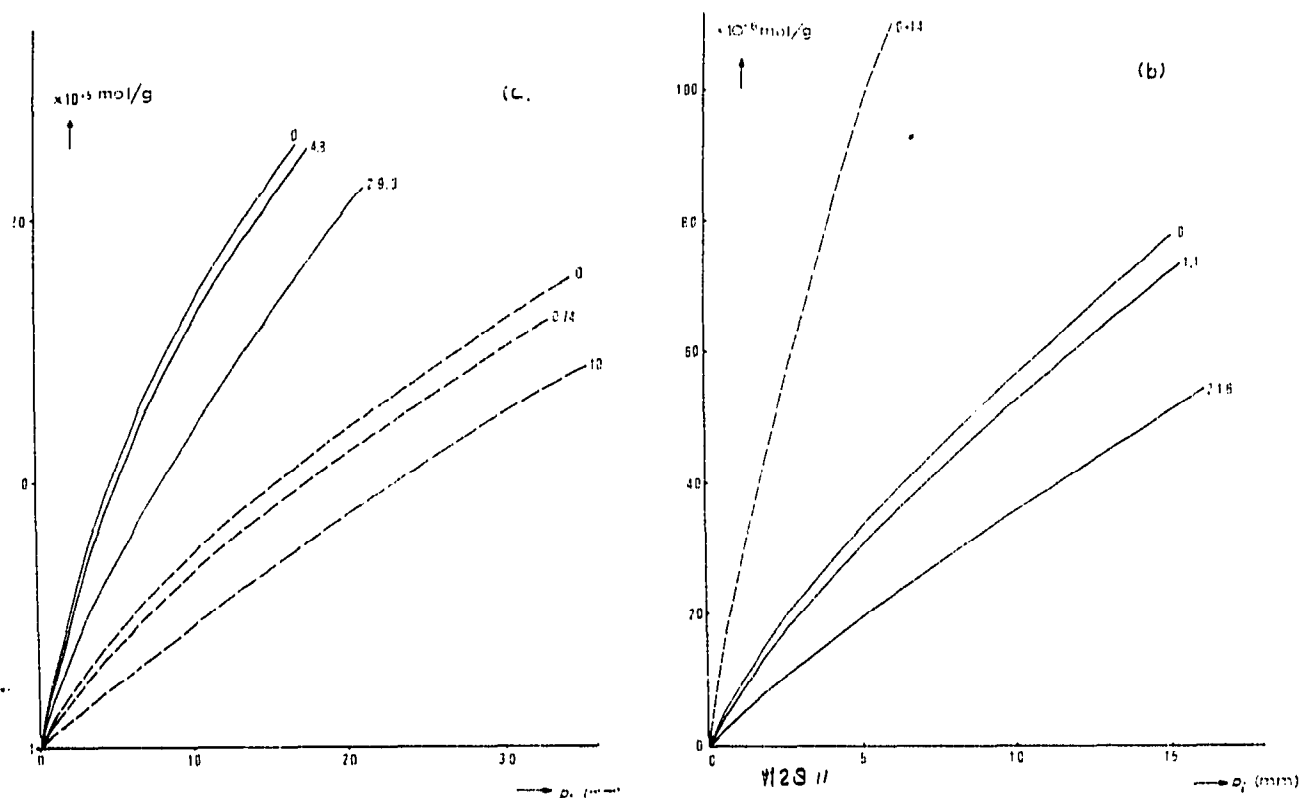


Fig. 12. Simultaneous adsorption of binary mixtures on Porapak Q at 100°. Plot as in Fig. 7.

	<i>i</i>	<i>j</i>
(a) (— — — —)	hexane	pentane
(- - - -)	pentane	hexane
(b) (- - - -)	benzene	acetone
(— — — —)	acetone	benzene

A linear relationship between the concentrations in the surface layer at constant pressure of one adsorbate is found on silica for benzene with acetone as non-isobaric component and for hexane with acetone or benzene as non-isobaric component, as can be seen from Fig. 11. The curves for hexane with acetone or benzene as non-isobaric component coincide for the same vapour pressure of hexane. This can be expected according to eqn. 7 ($C_i, C_j = \text{constant}$ and $N_i^z, N_j^z = \text{constant}$).

Adsorption of binary gas mixtures on hydrophobic solid surfaces. The adsorption of acetone–benzene and hexane–pentane mixtures on Porapak Q at 100° has been studied. According to the chemical properties of its surface, Porapak Q has adsorption characteristics that are the reverse of those of hydrophilic adsorbents towards polar and non-polar compounds, as is demonstrated in Figs. 12a and b for the binary mixtures pentane–hexane and benzene–acetone. On Porapak Q, the adsorption functions $c_i^\sigma = f(c_j^\sigma)_{T, p_i}$ are linear for pentane–hexane mixtures with either pentane or hexane as the isobaric compound (Fig. 13). The slopes of the curves are equal, which can be explained by eqns. 7a and b, assuming $C_i, C_j \ll N_i^z, N_j^z$. The corresponding curve for acetone on Porapak Q with benzene as the non-isobaric component has a slope that gradually approaches zero. This can be explained by assuming acetone to be increasingly adsorbed on benzene.

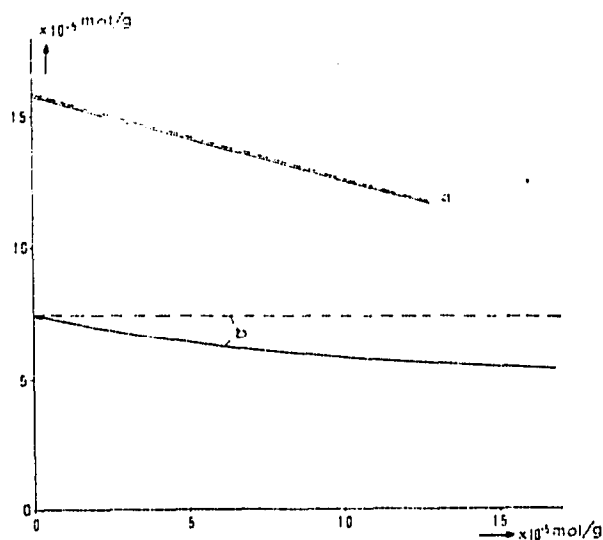


Fig. 13. Simultaneous adsorption of binary mixtures on Porapak Q at 100°. Plot as in Fig. 8.

	<i>i</i>	<i>j</i>	p_i (mm)
(a) (---)	pentane	hexane	28
(- - - -)	hexane	pentane	8
(b) (---)	benzene	acetone	0.3
(- - - -)	acetone	benzene	1.1

CONCLUSIONS

As can be seen from Figs. 8, 11 and 13, the sorption of the component *i* at constant partial pressure p_i decreases with increasing sorption of the other component *j*. The sorption of component *i* changes gradually from adsorption on the solid surface to dissolution in a liquid film of component *j*. Approaching dissolution, it may be expected that the concentration of the isobaric compound (in moles per unit mass of solid) will tend to increase linearly with the concentration of the non-isobaric compound (in moles per unit mass of solid). Any deviation from this linear relationship must be caused by adsorption on the solid-liquid and liquid-gas interfaces. This phenomenon will be discussed in a following paper, especially in relation to the accuracy of GC retention data.

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