GAS CHROMATOGRAPHIC DETERMINATION OF ORGANIC VAPOURS AND INORGANIC AEROSOLS IN NONCORROSIVE GASES SORPTION OF GASES BY GRANULATED SORBENTS TO DYNAMIC EQUILIBRIUM — THE DUBININ–RADUSHKEVICH EQUATION

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Dedicated to Professor F. Čůta on the occasion of his 80th birthday.

A universal method is suggested for an objective evaluation of the utility of microporous sorbents for the sampling of organic vapours up to the dynamic equilibrium. It is based on an analysis of the Dubinin–Radushkevich isotherm set up from the adsorption data for the standard adsorbate chosen (benzene). The theoretical approach was verified experimentally with active carbon. Based on the results, a procedure was worked out for the analysis of environmental atmosphere and noncorrosive gases containing impurities of some nonpolar organic solvent vapours in the presence of humidity, for a concentration region corresponding to the relative pressures of 10^{-4} to 10^{-2}. The gas analyzed is aspirated through an allonge containing 6 g of a molecular sieve 3 A and a column of 10 mg of active carbon for 50 min with the flow rate of $1 \, l \, min^{-1}$. After the sampling, the nonpolar substances are desorbed using either an inert gas at elevated temperature or carbon disulfide. The eluate is analyzed by gas chromatography.

For the determination of low concentrations (10^{-1}—10^{-4} mol m^{-3}) or organic vapours present in noncorrosive gases or as pollutants in air, it is first necessary to obtain a representative sample by means of a defined procedure. The sampling must be reproducible, it should conform to the limit of detection of the gas chromatographic determination applied, and the desorption should be simple and quantitative. While quantitative sampling by nonequilibrium physical adsorption on granulated sorbents is routine[1,2], sampling up to the dynamic sorption equilibrium has not yet found widespread application. Several techniques of sampling up to dynamic gas–liquid partition equilibrium have been described. Novák and coworkers[3] used a method of organic vapour sampling up to the dynamic equilibrium on the silicone elastomer E-301 and polyethylene-glycol 400 on Celite support, placed in a short tube. The authors report the limit of determination of $4 \cdot 2 \, . \, 10^{-8}$ mol m^{-3} and the error of 5% for the optimum concentration region of $4 \cdot 2 \, . \, 10^{-5}$ to $1 \cdot 0 \, . \, 10^{-3}$ mol m^{-3}. Dravnieks and coworkers[4] performed the sampling to equilibrium in a stainless column containing methylsilicone SF-96 on Chromosorb 102; they reached the limit of chromatographic determination of $1 \cdot 4 \, . \, 10^{-8}$ mol m^{-3}. The author published also a paper[5] dealing with the equilibrium sampling in a small fluid cyclone on Apiezon L with Fluoropak 80 as the support, and obtained the limit of determination of the method $4 \cdot 2 \, . \, 10^{-8}$ mol m^{-3}. Equilibrium dynamic adsorption in a liquid was employed for sampling by Ioffe and coworkers[6]. Using a small glass impinger with 1·5—3 ml of acetic acid, the authors attained the average

limit of determination for carbonyl compounds and diethylamine $1·4 . 10^{-6}$ mol m^{-3}. Dravnieks and Krotoszynski[7] made use of the partition equilibrium between a thin film of an organic liquid fixed on the inner surface of a Pyrex coil. Applying Apiezon L and polyethylene glycol adipate they obtained the limit of determination $1·7 . 10^{-8}$ mol l^{-1}. The conditions for an analytical application of gas–liquid partition equilibria were dealt with from the theoretical point of view by Novák and coworkers[3] and later by Ioffe and coworkers[8]; a sufficient volume of the requisite data are available. The values of the distribution coefficients must be calculated from the experimental chromatographic data prior to the sampling. While the gas–liquid partition isotherms are commonly linear, the adsorption isotherms of microporous adsorbents possess usually a characteristic convex shape, and their general analytical expression is more complex, particularly if water vapours are present. Despite this drawback, the study of equilibrium sorption is of analytical importance as shown by Janák and coworkers[9]. These authors have studied the possibility of analysis of gases by sorption of vapours of polar as well as nonpolar solvents (methanol, ethanol, propanol, ethyl acetate, acetone, and benzene) in the presence of water vapours up to the dynamic sorption equilibrium on a column of granulated Tenax-GC (2,6-diphenyl-1,4-phenylene oxide) (60—80 mesh). They have found that the presence of water vapours in the gas analyzed with the adsorbate concentrations up to $4·5 . 10^{-4}$ mol m^{-3} did not bring about changes in the sorption properties of the Tenax exceeding $±10\%$, in which this sorbent is superior to other sorbents such as active carbon or silica gel. Based on these findings, the above authors suggest sampling to the dynamic equilibrium without a prior drying of the gas to be analyzed; for the determination of, *e.g.*, acetone as air pollutant, they recommend the use of 250 mg of Tenax in a Teflon sampling tube. Unlike the methods based on nonequilibrium sorption, the sampling up to the equilibrium requires neither precise measurements of the volume of the aspirated gas nor a large amount of the sampling sorbent, particularly if organic substances possessing a low boiling point are being trapped.

In this paper we suggest a method for the evaluation of the utility of microporous sorbents for sampling of organic vapours up to the equilibrium, based on an analysis of the set up Dubinin–Radushkevich equation. With this equation it is possible to calculate the adsorption isotherms of sorbates at various temperatures from the measured or calculated coefficients of affinity β. The theoretical conclusions were tested with granulated active carbon, a typical representative of microporous sorbents.

THEORETICAL

If the analytical form of the adsorption isotherm is known, then the equilibrium sorbed amount, expressed as the adsorbate concentration in a weight unit of the sorbent (C_s), can be employed as the analytical property for the analysis of gaseous mixtures. When the equilibrium sorbed amount of the substance is determined by analysis, the adsorbate concentration in the gaseous phase can be uniquely calculated from the equation of the isotherm. Of a series of analytically expressed isotherms, the characteristic curves $W = f(A)$* based on the potential theory of sorption turned out to be the most suitable for analytical purposes. When the gaseous phase, with the

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*   See the attached List of symbols.

adsorbate concentration C_g, is in contact with a first structural type sorbent[10], then after a time a dynamic equilibrium establishes, characterized by the filling of the adsorption space of the micropores W, which can be determined according to the relation

$$W = n v_T = n M / d_T = C_s / d_T . \tag{1}$$

The work, which is done by the adsorption forces during this process, denoted as the adsorption potential A, can be expressed by the relation

$$A = -\Delta G = RT \ln \left(C_{g0} / C_g \right) . \tag{2}$$

For the dependence $W = f(A)$, the approximate analytical expression

$$
\begin{aligned}
W &= W_0 \exp\left(-kA^2\right) \\
&= W_0 \exp\left\{-\left[BT^2/\beta^2\right]\left[\log\left(C_{g0}/C_g\right)\right]^2\right.
\end{aligned} \tag{3}
$$

is applicable in some limits; it has been suggested by Dubinin and is called the Dubinin–Radushkevich isotherm[10] of the sorbent concerned. Dubinin verified later experimentally that in some conditions this isotherm can acquire the properties defined by the relations

$$(\partial A/\partial T)_W = 0 \tag{4}$$

$$(\partial W/\partial T)_A = 0 \tag{5}$$

$$(A/A_r)_W = \beta . \tag{6}$$

If these are satisfied, it is possible to determine the adsorption isotherm of a substance at some temperature from a single experimental characteristic curve for a reference standard adsorbate (benzene) at a chosen temperature.

The constant β is a measure of adsorbability of the organic vapour in question on a microporous sorbent, and is independent of the structure of the micropores[11]. This constant is usually termed[12,13] the coefficient of affinity, and according to Dubinin[14] expresses the relative differential molar work of vapour adsorption with the chosen standard substance. Dubinin claims[15] that the relation (6) is obeyed for microporous sorbents (active carbon, silica gel) in the region of relative pressures of 10^{-5} to 10^{-1}. Dubinin and Timofeev[11] have also shown that the coefficient of affinity β can be in many cases calculated with a good accuracy from some non-adsorption physical data, from the parachors for instance:

$$b = P/P_r = \left[v_T(\gamma_T)^{1/4}\right]/\left[v_{rT}(\gamma_{rT})^{1/4}\right] . \tag{7}$$

The span of the adsorbate concentrations in the gaseous phase in that Eq. (3) holds true, is a measure of the analytical utility of a sorbent for sorption up to the dynamic equilibrium.

EXPERIMENTAL

Chemicals and Apparatus

Active carbon HS (Moravian Chemical Works, Ostrava), specific surface $1200—1300 \text{ m}^2 \text{ g}^{-1}$. Carbon disulfide *p.a.* (Riedl de Haën) was purified by 24 hour's standing with nitration mixture (1 part of the nitration mixture $+10$ parts of CS_2) and redistillation. The organic solvents (*p.a.*) were freshly redistilled and their purity was tested by gas chromatography. Molecular sieve 3 A (G. Dimitrov Chemical Works, Bratislava), beads 1 mm, were regenerated at 400°C in a stream of dry nitrogen, from which the humidity was frozen out at —72°C. Calcium carbide (technical product), fraction $0·5—2·0$ mm. Gas chromatograph Argon Pye 12103 (Pye Unicam, Cambridge), glass column $1·5$ m $\times$ 4 mm i.d., packed with Chromosorb W with 10% polyethylene glycol 20 M. The flow rates of nitrogen, hydrogen, and air were 30, 25, and 300 ml min^{-1}, respectively. The working temperature was 65°C for the analysis of the eluates and 100°C during the measurements of the adsorption data.

Apparatus for the Adsorption Data Measurements

The apparatus (Fig. 1) enabled a continual (at least for 40 h) preparation of gaseous mixtures of liquid organic substances in nitrogen with the relative humidity from 0 to 90%. For flow rates from $0·02$ to $2·5$ l min^{-1} it was possible to prepare concentrations of the organic substances in the gaseous phase corresponding to the relative pressures of 10^{-5} to 10^{-1}. When the dynamic equilibrium established, the concentration variations did not exceed $\pm4\%$. In the saturators, a gaseous mixture was prepared with a high concentration of the organic substance vapour in dry nitrogen (flow rate $1—30$ ml min^{-1}), according to the inner diameter of the capillary used in the mixer. In the ejection mixer the vapours of the organic substance were diluted either with dry nitrogen or with nitrogen of a preselected humidity, to give a mixture of the required concentration and humidity. The desired nitrogen humidity was achieved by mixing streams of dry nitrogen and nitrogen of 90% relative humidity in a capillary mixer, and was proportional to the ratio of the flow rates, as read off on the flow meters. The gaseous mixture of the resultant concentration and relative humidity was kept at the temperature of 20°C in a tube containing glass beads, and GC analyzed before and after the adsorption. The himudity of the diluting nitrogen stream was monitored prior to the mixing with the organic vapour by recording the peaks of the ethine evolved from the calcium carbide in the reaction tube. The apparatus was calibrated by determining the weight of the organic vapour adsorbed on the active carbon after the flow of a chosen volume of the gaseous mixture through the weighed adsorption tube, with a preselected setting of the needle valve. The quantitativeness of sorption of the organic substance vapour was checked chromatographically. In the calibration graph, the heights of the peaks obtained on the injection of the gaseous mixture were plotted for the various flow rates *versus* the concentration in the gaseous phase, calculated from the weight of the adsorbed vapour. The apparatus for the adjustment of the relative humidity was calibrated analogously, the water vapour being adsorbed by the molecular sieve 3 A. The calibration plot represented the dependence of the relative humidity on the ratio of the flow rates read off from the flow meters.

Preparation of the Adsorption Tubes

As the adsorption tube served a glass tube, length 60 mm, inner diameter 6·00 mm and reduced near one end, equipped with ground joints. The adsorption bed was fixed by two hollow brass rollers, tightly bearing on the tube walls. The rollers were closed on one side by screens, mesh size 0·01 mm². The adsorbent was active carbon, fraction 1·0—1·2 mm, freed from dust by five- to tenfold decantation with cold and hot distilled water and dried in a nitrogen stream at 110°C for 12 h. The stock portion was stored in a dessicator over silica gel with an indicator. Before each experiment, the active carbon in the adsorption tube was degassed at 250—300°C in a dry nitrogen stream until constant weight was attained.
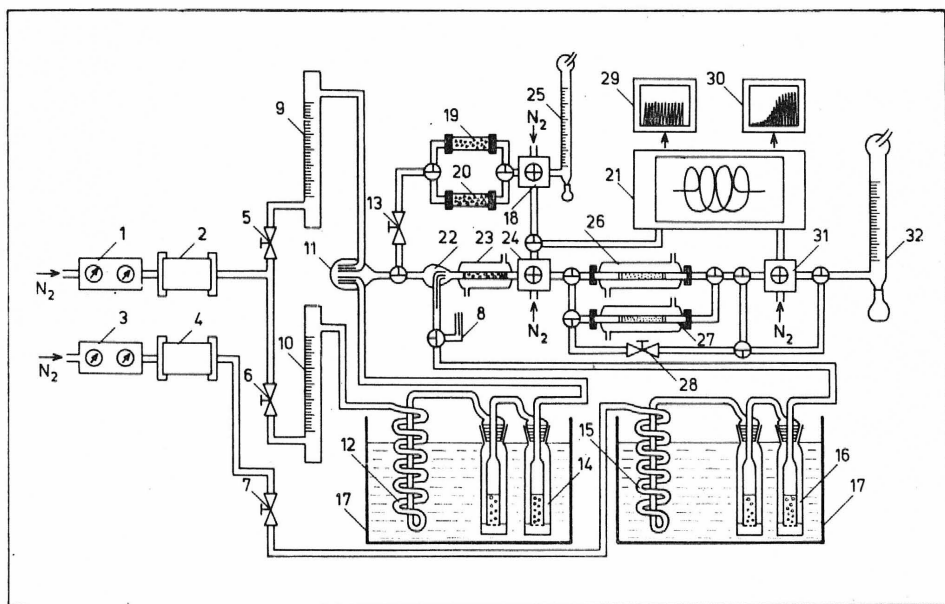

FIG. 1

Apparatus for the Preparation of Defined Concentrations of Organic Vapours in Nitrogen With a Chosen Relative Humidity

1, 3 Flow rate and pressure controllers, 2, 4 blocks of molecular sieves, 5, 6, 7, 13, 28 needle microvalves with scale, 9, 10 rotameters, 11 capillary mixer, 12, 15 temperature controlling coils, 14 saturators of nitrogen with water vapour, 16 saturators of nitrogen with the organic vapour, 17 ultrathermostats, 8 closing cock with a capillary communicating with the atmosphere, 18, 24, 31 flow-through dosing valves, 19, 20 generation tube with calcium carbide, 22 ejection mixer, 23 temperature controlled antilaminarization tube with glass beads, 26, 27 temperature controlled beds with the adsorption tubes, 21 gas chromatograph, 29, 30 compensation recorders, 25, 32 bubble flow meters.

Procedure for the Determination of the Adsorption and Kinetic Data

The gaseous mixture of the given concentration of the organic vapour was aspirated through the weighed adsorption tube with the layer of degassed active carbon, placed in the jacket, until the equilibrium adsorption was attained (peaks of constant height were recorded and the weight of the adsorption tube did not vary). From the breakthrough curve obtained, the time periods required for the establishing of the equilibrium were determined for the various flow rates; the increment of the weight of the adsorption tube gave the equilibrium sorbed amount of the substance per weight unit of the sorbent (C_s).

Analysis of the Sorbent

The desorption of higher-boiling organic substances trapped on the active carbon was performed with carbon disulfide[2] immediately in the adsorption tube. In the tube was placed a glass wool plug wetted with several drops of carbon disulfide. The adsorption tube, connected to the funnel by means of a silicone rubber tube, was repeatedly washed in 5 min intervals with 0·5 ml portions of chilled (0°C) carbon disulfide, and the eluate was collected in a graduated cylinder recalibrated to filling under cooling. The elution was stopped when the total volume of the eluate amounted to 4 ml. The internal standard was added, the mixture was diluted to the volume of 5 ml, and a 5 μl portion of the solution was chromatographed. The desorption of low-boiling adsorbates was carried out by using a stream of nitrogen at the temperature of 250°C. The adsorption tube was placed in a stainless tube with threaded ends equipped with Teflon gaskets. The stainless tube was placed in a heating box for 2 min; after that time the desorbed substance was flushed into the gas chromatograph by means of a by-pass device. The peaks were evaluated planimetrically.

Preparation of the solutions. The stock solutions were prepared by dissolving 0·1 g of the organic substance in 10 ml of carbon disulfide. The standard solutions were obtained by diluting the stock solutions twenty five times. The stock solution of the internal standard in carbon disulfide was obtained by dissolving 0·16 g of toluene in 10 ml of the solvent, and the standard solution was prepared by tenfold dilution of this stock solution.

The calibration curve. The peak heights of the organic substances and of the internal standard were measured and their ratios were calculated (internal standard = 1). The values obtained were plotted *versus* the concentration of the substances to be determined.

RESULTS AND DISCUSSION

The adsorption isotherms of benzene, dichloromethane, trichloromethane, and tetrachloromethane measured at 20°C are shown in Fig. 2. From their shape it follows that they belong to the adsorption isotherms of the first type according to the Brunauer classification[16], which are characteristic of microporous sorbents and that are likely to obey relations based on the potential energy of sorption. In Fig. 3, the curves of the Dubinin–Radushkevich equation in the rectified form

$$\log W = \log W_0 - [BT^2/\beta^2 \ln 10]\left[\log\left(C_{g0}/C_g\right)\right]^2 \tag{8}$$

are plotted in the coordinates $\log W$ and $\left[\log\left(C_{g0}/C_g\right)\right]^2$. For $\left[\log\left(C_{g0}/C_g\right)\right]^2 = 4$

to 16 the plots are seen to be linear, hence for adsorbate concentrations corresponding to relative pressures 10^{-4} to 10^{-2} the condition that the coefficient of affinity be constant (Eq. (6)) is met. The extrapolated linear parts of the curves form the abscissa intercept of $\log W_0 = -0.41$, which corresponds to the limiting micropore volume $W_0 = 0.389 \text{ cm}^3 \text{ g}^{-1}$. From the slope of the linear part of the rectified curve calculated by the least squares method, the value of the second constant $B = 1.25 \cdot 10^{-6} \text{ K}^{-2}$ was obtained. Dubinin and coworkers[17] report the B values of $0.2 \cdot 10^{-6}$ to $3 \cdot 10^{-6} \text{ K}^{-2}$ for various microporous sorbents. Furthermore, variations in the temperature term T^2 in Eq. (3) were tested to be well compensated for by the term $[\log (C_{g0}/C_g)]^2$ as a result of changes in the saturated vapour pressure with the temperature, the relations (4) and (5) being satisfied. The coefficients of affinity β calculated from the slopes of the rectified curves of the adsorbates in question, along with the published data and values calculated according to Eq. (7), are summarized in Table I. The measured coefficients of affinity for the active carbon HS are in a good agreement with the data published for other types of active carbon. With regard to the analytical applications of this work, the coefficients of affinity of some nonpolar substances measured by other authors are included in Table I, too. The error of the approximate calculation of the coefficients of affinity from the parachors (Eq. (7)) is up to 7%.
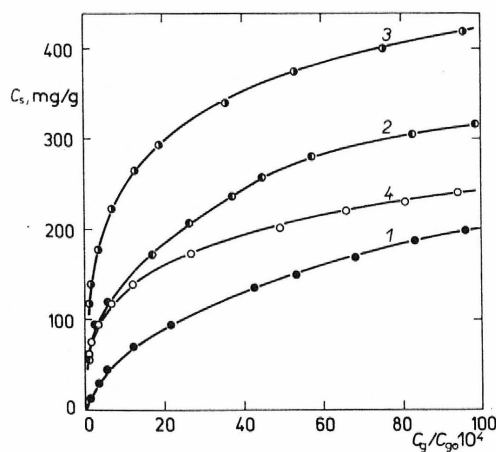

FIG. 2

Adsorption Isotherms on the Active Carbon HS at 20°C

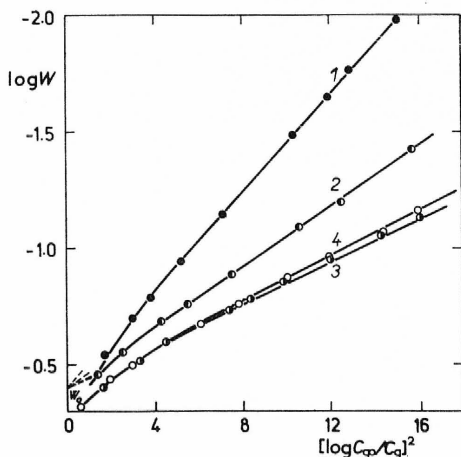1 Dichloromethane, 2 trichloromethane, 3 tetrachloromethane, 4 benzene.

FIG. 3

Rectified Dubinin-Radushkevich Isotherms at 20°C for the Active Carbon HS

1 Dichloromethane, 2 trichloromethane, 3 tetrachloromethane, 4 benzene; W in $\text{cm}^3 \text{ g}^{-1}$.

The Dubinin–Radushkevich equation set up for active carbon is applicable, as found by analysis, to the determination of organic substances in noncorrosive gases or as air pollutants in the concentration region corresponding to the relative pressures of 10^{-4} to 10^{-2} at temperatures up to $0.3 T_K$ (for benzene, $T_K = 561$ K). For analytical purposes, the concentration of the adsorbate in the gaseous phase was expressed explicit from Eq. (3): the relation

$$C_g = C_{g0} \exp \left\{ -(\beta \ln 10/T) \left[\ln \left(W_c d_T/C_s \right)/B \right]^{1/2} \right\} \qquad (9)$$

was obtained by employing Eq. (1). The numerical values of the constants W_0 and B as determined for the active carbon used were inserted to obtain the form

$$C_g = C_{g0} \exp \left\{ -(2.055 \cdot 10^3 \beta/T) \left[\ln \left(d_T/C_s \right) - 0.9441 \right]^{1/2} \right\} \qquad (10)$$

suitable for analytical calculations. C_{g0} was then calculated from the saturated vapour pressure of the adsorbate under study, P_{g0}, according to the modified equation of state

$$C_{g0} = M P_{g0}/RT \qquad (11)$$

TABLE I
Observed (β_{obs}), Published (β_{pub}), and Calculated (β_{cal}) Coefficients of Affinity
Calculations performed according to Eq. (7).

Adsorbate	β_{obs}	β_{pub}	β_{cal}	Departure of the calculation %
Dichloromethane	0·67	0·66[a]	0·71	+5·9
Trichloromethane	0·85	0·86[a]	0·89	+4·7
Tetrachloromethane	1·01	0·96[b]	1·06	+4·9
Benzene	1·00	1·00[a]	1·00	—
Toluene	—	1·25[a]	1·19	−4·8
Diethyl ether	—	1·09[a]	1·02	−6·4
n-Pentane	—	1·08[b]	1·02	−5·6
n-Hexane	—	1·35[a]	1·31	−2·9
n-Heptane	—	1·59[a]	1·61	−5·0

[a] Dubinin and Timofeev[11]; [b] Dubinin and coworkers[18].

Working procedure. A column of 10 mg of the degassed active carbon was prepared in the adsorption tube. To the tube was connected an allonge with 6 g of the molecular sieve 3 A and the gas to be analyzed was aspirated with the flow rate of 800—1 200 $cm^3 min^{-1}$ for 50 minutes. After the sampling, the temperature of the mixture analyzed was measured. Variations in the flow rate are not a hindrance and the volume of the gas passing need not be measured. Adsorbates possessing lower boiling points were desorbed with nitrogen at 250°C, for those possessing a higher boiling point, carbon disulfide was applied. The amount of the adsorbate found by analysis was recalculated to 1 g of the active carbon (C_s) and the concentration of the adsorbate in the gas analyzed was obtained by employing the relation (*10*).

The amount of the molecular sieve used is capable of quantitative sorption of the water vapour from the gas analyzed possessing 90% relative humidity for 60 minutes (when the concentration of the water vapour in the gas is 15·6 mg l^{-1}, which represents 90% humidity at 20°C, 194 mg of H_2O is sorbed to equilibrium on 1 g of the sieve). It was verified that the molecular sieve 3 A did not sorb the substances given in Table I, as was also anticipated based on the effective radii of the molecules. The analysis of the breakthrough curves also evidenced that at the flow rate 1 l min^{-1}, the dynamic equilibrium on 10 mg of the active carbon established for the substances of Table I in 15 to 40 minutes. If the flow rate, temperature, and weight and geometrical arrangement of the sorbent are regarded as constant, then the time required for the establishing of the dynamic equilibrium is dependent upon the adsorbate concentration in the gaseous phase and on the value of the coefficient of affinity β. The breakthrough curves obtained for benzene concentrations corresponding to the relative pressures of 10^{-4} to 10^{-2} are shown in Fig. 4. For the experimental coefficient of affinity, the method suggested exhibits the reproducibility characterized by the standard deviation of 10−15% for concentrations corresponding to the relative pressures of about 10^{-4}, and 6−9% (9 determinations) for concentrations corresponding to the relative pressures near 10^{-2}, according to the kind of the adsorbate.
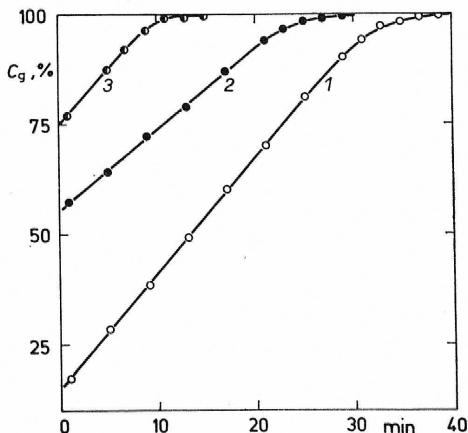

FIG. 4

Breakthrough Curves of Benzene

10 mg of the active carbon HS, fraction 1·0—1·2 mm, flow rate 1000 $cm^3 min^{-1}$, benzene concentration: *1* $10^{-4}C_{g0}$, *2* $10^{-3}C_{g0}$, *3* $10^{-2}C_{g0}$ ($C_{g0} = 318\cdot8$ l l^{-1}); inner diameter of the adsorption tube 6·00 mm.

The reproducibility of determination depends considerably on the quantitativeness of the desorption. With carbon disulfide, all the substances given in Table I can be desorbed in the arrangement suggested with a yield of at least 96%. Desorption with a stream of nitrogen at 250°C, suitable for n-pentane, diethyl ether, and dichloromethane, proceeds in the arrangement in question with a yield not lower than 97%. If the coefficients of affinity calculated from the parachors are used (if the experimental values are not available from the literature), a lower accuracy of the results is to be expected. The limit of determination of the method is given by the adsorbate concentration corresponding to the relative pressures of 10^{-4}, which for benzene makes $4 . 10^{-4}$ mol m^{-3}.

LIST OF SYMBOLS

A	adsorption potential (cal mol^{-1})
A_r	adsorption potential of benzene (cal mol^{-1})
B	a constant (K^{-2})
C_g	adsorbate concentration in the gaseous phase (g cm^{-3})
C_{g0}	adsorbate concentration in the gaseous phase corresponding to the saturated vapour pressure at the temperature T (g cm^{-3})
C_s	adsorbate concentration in a weight unit of the sorbent (g g^{-1})
d_T	density of the liquid adsorbate at the temperature T (g cm^{-3})
ΔG	standard change of molar free enthalpy (cal mol^{-1})
k	a constant (mol^2 cal^{-2})
M	molecular weight of the adsorbate (g mol^{-1})
n	mass amount of the adsorbate in a weight unit of the sorbent (mol g^{-1})
P	parachor of the adsorbate (dyn$^{1/4}$ cm$^{11/4}$ mol^{-1})
P_{g0}	saturated vapour pressure of the adsorbate at the temperature T (Torr)
P_r	parachor of benzene (dyn$^{1/4}$ cm$^{11/4}$ mol^{-1})
R	universal gas constant (6·2358 . 10^4 Torr cm^3 mol^{-1} K^{-1})
T	adsorption temperature (K)
T_k	adsorbate critical temperature (K)
v_{rT}	molar volume of liquid benzene at the temperature T (cm^3 mol^{-1})
v_T	molar volume of the liquid adsorbate at the temperature T (cm^3 mol^{-1})
W	adsorption space of the sorbent (cm^3 g^{-1})
W_0	limiting adsorption space of the sorbent (cm^3 g^{-1})
β	coefficient of affinity (*1*)
γ_{rT}	surface tension of benzene at the temperature T (dyn cm^{-1})
γ_T	surface tension of the adsorbate at the temperature T (dyn cm^{-1})

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Translated by P. Adámek.