Bei der Polystyrol-Selenin-Säure (Abb. 1 d) und bei der Polystyrol-Phosphin-Säure (Abb. 1 e) findet man, auch wenn sich diese bei 98% relativer Luftfeuchtigkeit hydratisiert hat, nur $-$SeOOH (VIII)- und $-$PHOOH (X)-Gruppen. Hiermit ist der Grad der wahren Dissoziation dieser Säuren sehr klein.

Der Grad der wahren Dissoziation zeigt hiernach in Abhängigkeit von der Art des Anions einen charakteristischen Gang. Er nimmt von der Polystyrol-Sulfon-Säure zur Polystyrol-Phosphin-Säure ab. Dieser Gang steht in engem Zusammenhang mit der beobachteten Vergrößerung der Mesomerie in den Anionen, die bei Ablösung des Protons eintritt[8]. Außerdem ist die Umordnung der Säure-Gruppen für die Assoziation dieser Gruppen von wesentlicher Bedeutung, denn bei dieser Umordnung erhalten die nun doppeltgebundenen O-Atome eine beträchtliche Wasserstoff-Brücken-Akzeptor-Eigenschaft (siehe hierzu ZUNDEL, METZGER und SCHEUING[9]).

Ich danke der Deutschen Forschungsgemeinschaft für die Mittel, welche für die Durchführung dieser Arbeit notwendig waren.

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Gas-Solid Interaction: Study of the Systems C_6H_6—γ-Al_2O_3, CCl_4—γ-Al_2O_3 and cyclo-C_6H_{12}—γ-Al_2O_3 by Means of the B.D.D.T. Equation *

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(Z. Naturforschg. **22 a**, 203—207 [1967]; received 27 October 1966)

Gas-solid adsorption was experimentally investigated at 25 °C for the title systems, which all exhibit isotherms of type IV with a hysteresis loop.

The B.D.D.T. equation was employed for the treatment of the experimental data, and the values obtained for its four constants have been discussed and compared with values derived by independent methods. In particular, for $C_6H_6-\gamma$-Al_2O_3 a good agreement was found between the calculated value of the interaction energy in monolayer and calorimetric data.

Among the different types of VAN DER WAALS adsorption, the systems showing multilayer adsorption complicated by capillary condensation (type IV isotherms) have not been extensively investigated so far[1].

The only general kinetic theory available for these cases is that of B.D.D.T.[2]. By a generalization of the B.E.T. procedure[3], these authors derived a rather complicated relation between a (amount of adsorbed gas) and $x \equiv p_R$ (relative pressure) of the form

$$a = a_m \cdot f(x, C, n, g) \tag{1}$$

where

a_m = amount absorbed in a completed monolayer;

$$C = \exp\{(E_1 - E_L)/RT\}; \tag{2}$$

with

E_1 = average interaction energy[4] of monolayer with solid surface

and

E_L = heat of vaporization of the liquid;

n = maximum number of layers that can be absorbed (as an average) between the capillary pore walls;

$$g = \exp(Q/RT). \tag{3}$$

Q has been defined by B.D.D.T. as "an additional energy of adsorption" for the last layer, i. e. that which fills the pores to completion.

Eq. (1), which contains four unknown parameters (a_m, C, n, and g), has received very few practical applications up-to-day[5]. Two simplified procedures have been proposed: the first, adopted in the origi-

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nal B.D.D.T. paper, employs an approximated form of Eq. (1); the second, as suggested by CLAMPITT and GERMAN[6], involves a further simplification of Eq. (1) and requires an independent value for Q (and consequently for g) which might be obtained from surface tension data.

In this work, adsorption and desorption experiments have been carried out, at 25 °C, on the systems formed with C_6H_6, CCl_4 and cyclo-C_6H_{12} respectively and γ-Al_2O_3. The data have been treated by a suitable procedure, employing the complete form of Eq. (1).

Experimental

Apparatus and procedure. The apparatus was a version of those commonly employed in the conventional gravimetric method (see, e. g., ORR[7]). The principal part was an adsorption chamber, thermostated and fitted with a mercury manometer, so designed as to allow the easy opening and closing, from outside, of the adsorption bulb therein contained. Each point of an isotherm was determined by closing the bulb after equilibrium pressure was reached, withdrawing it from the chamber and weighing.

Materials. The liquids used to produce the adsorbate vapours were from C. Erba S. p. A. (Milan): C_6H_6, RS grade; CCl_4, RP grade; and cyclo-C_6H_{12}, RS "spectrophotometric grade". They were carefully dried and repeatedly distilled by standard methods, and showed values of the refractive index in close agreement with literature.

The solid adsorbent was a sample of γ-Al_2O_3 "for chromatographic adsorption analysis" from B.D.H. Ltd., possessing a specific surface area of 95 m^2/g (as determined by the argon method with an ATLAS BET-o-graph) and grain size ranging for 85% from 60 to 90 μ. The adsorbent, previously heated at 300 °C for 24 hours, was furtherly heated in the adsorption chamber at 130 °C under a pressure of $\sim 10^{-5}$ Torr for 8 hours immediately before each experimental run. Such a procedure ensured reproducibility of surface activation[8].

Results. Several runs were carried out with each system, both in the adsorption and in the desorption branch of the corresponding isotherms. The results are reported in Tables 1, 2 and 3. For the calculation of p_R from pressure measurements, the following values were taken from literature for the vapour pressures at 25 °C: C_6H_6, 93.86[9]; CCl_4, 113.9 (by interpolation of

Run	p_R	a (mg/g)	Run	p_R	a (mg/g)
1 a	0.0236	9.9	2 a	0.0922	19.8
	0.0697	16.5		0.1127	22.5
	0.1322	26.1		0.1189	24.6
	0.2080	39.5		0.1568	31.2
	0.2921	59.3		0.1722	34.5
	0.3566	74.4		0.1804	36.1
	0.4427	96.0		0.2316	46.0
	0.7102	129.7		0.2910	60.4
1 d	0.6477	133.0		0.3167	66.5
	0.5042	122.9		0.3863	87.1
	0.3966	110.7		0.5134	111.4
	0.3371	92.1		0.6395	125.9
	0.2900	79.8		0.6774	131.4
	0.2623	68.7	2 d	0.4355	113.7
	0.2357	56.6		0.3617	101.2
	0.2090	45.2		0.3095	85.7
	0.1875	38.6		0.2808	73.0
2 a	0.0533	13.4		0.2470	59.4
				0.1916	39.4

Table 1. Experimental results for cyclohexane on γ-Al_2O_3 at 25 °C. a = adsorption, d = desorption.

Run	p_R	a (mg/g)	Run	p_R	a (mg/g)
1 a	0.0887	64.1	2 a	0.0492	44.4
	0.1563	86.9		0.0746	55.1
	0.4706	213.4		0.0904	63.5
	0.5935	241.2		0.1168	71.9
	0.7419	274.2		0.1370	78.5
1 d	0.7103	288.9		0.1870	93.4
	0.5680	269.0		0.2107	102.7
	0.4197	247.4		0.2467	116.6
	0.3213	216.1		0.3371	145.2
	0.2827	185.8		0.3758	171.0
	0.2572	161.5		0.4495	201.7
	0.2467	147.5	3 a	0.0263	18.5
	0.2309	135.9		0.2757	127.7
	0.2221	121.0		0.3986	173.5
	0.2168	112.4		0.5355	223.8
	0.1958	103.4		0.5707	232.2
2 a	0.0290	29.6		0.6636	257.0
	0.0325	34.1		0.7533	278.9

Table 2. Experimental results for carbon tetrachloride on γ-Al_2O_3 at 25 °C. a = adsorption, d = desorption.

Run	p_R	a (mg/g)	Run	p_R	a (mg/g)
1 a	0.0133	12.2	2 a	0.3537	91.5
	0.0213	17.4		0.4592	118.9
	0.0458	29.0		0.6414	148.2
	0.1022	37.7	3 a	0.0602	30.5
	0.2024	53.8		0.2301	60.5
	0.2770	72.1		0.3686	102.2
	0.3867	102.6		0.5146	131.9
	0.5028	128.6		0.8108	159.2
	0.7457	153.0	3 d	0.6872	159.0
2 a	0.0331	23.2		0.5210	146.3
	0.0916	36.8		0.3995	132.3
	0.1081	38.6		0.2834	93.0
				0.1854	56.2

Table 3. Experimental results for benzene on γ-Al_2O_3 at 25 °C. a = adsorption, d = desorption.

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several reported values[10, 11]); cyclo-C_6H_{12}, 97.58 Torr[12].

The form of the isotherms is shown in Fig. 1. The fair degree of reproducibility is apparent from the different runs reported in the tables. Some fluctuations were observed in a few cases for $p_R > 0.8$; for this reason, only the measurements in the range $0 \div 0.8$ have been taken as a basis for the following discussion.

Discussion

First of all it seems worth while considering the sensitivity of Eq. (1) to the changing in value of the single parameters C, g and n, the effect of a_m being apparent from the equation itself. To this end a number of generic isotherms have been calculated (by the aid of an IBM 7090 computer), with a common value for a_m, while each time two of the remaining parameters were held constant and the third was left free to change widely. The most significant results of this calculation are shown in Fig. 2: it may be seen that the first portion of the isotherms is mainly dependent on the value of C, while the g parameter is the controlling factor for the intermediate range, and the maximum number of layers, n, becomes influent on the end portion of the isotherms, where complete pore saturation is reached.

As shown previously[13], for very low p_R values Eq. (1) reduces to the classic B.E.T. equation[3] which contains only two constants. If this equation is applicable to the first portion of an actual isotherm a simple method is at hand for the evaluation of the parameters a_m and C. For the systems investigated in this work it was found that the range in which the linear B.E.T. equation is obeyed extends up to $p_R \cong 0.15$, as it is shown in Fig. 3. Linear plots of this kind for type IV isotherms have seldom been reported in the literature.

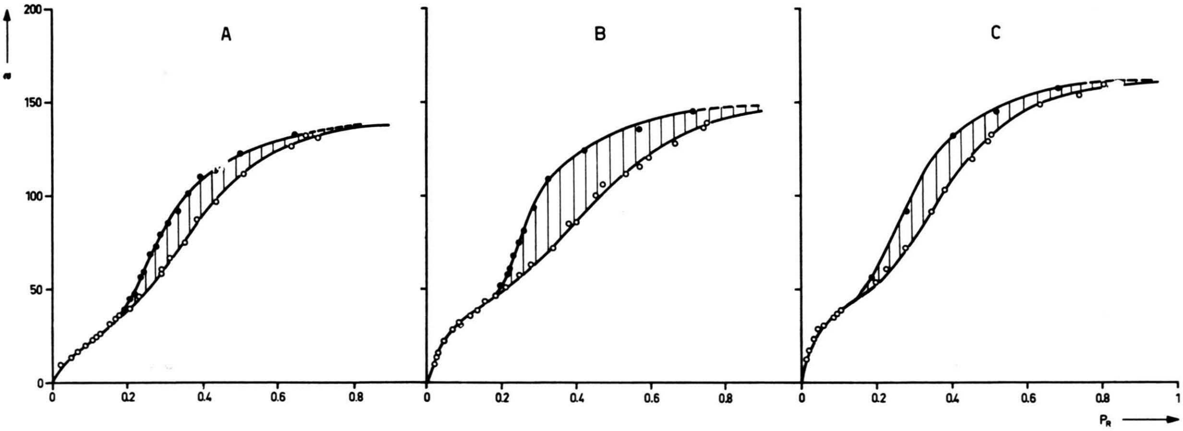

Fig. 1. Experimental adsorption and desorption isotherms for A = Cyclo-C_6H_{12}; B = CCl_4; C = C_6H_6 on γ-Al_2O_3 at 25 °C. ○ adsorption, ● desorption.

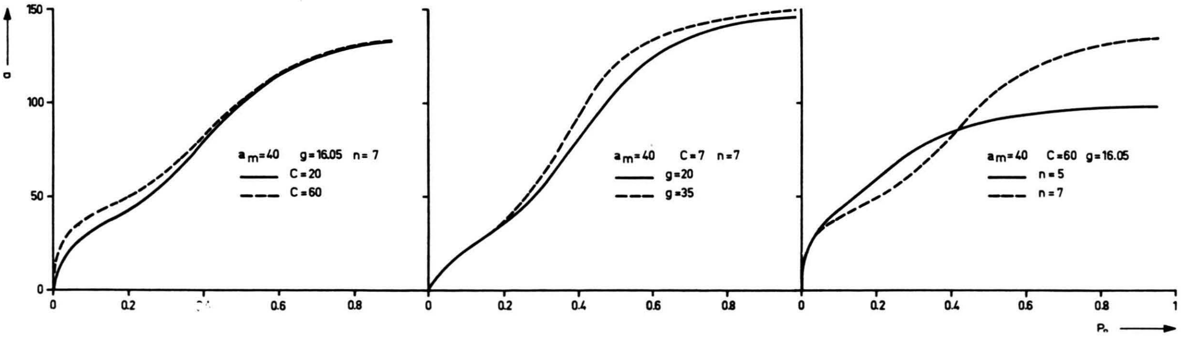

Fig. 2. Sensitivity of Eq. (1) to the changes of adsorption parameters.

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[13] See ref. [2], p. 1728.

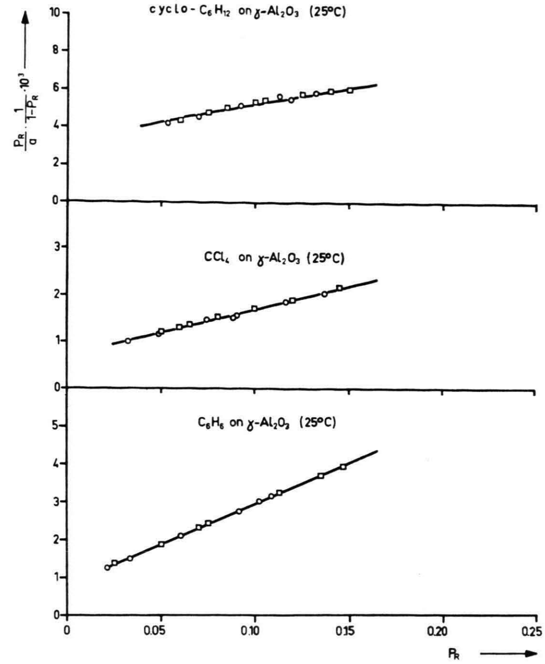

Fig. 3. Linear B.E.T. plots for cyclo-C_6H_{12}; CCl_4; C_6H_6. ○ experimental, ☐ interpolated.

adsorbate	a_m (mg/g)	C	g	n
cyclo-C_6H_{12}	43.98	6.87	25.00	6.50
CCl_4	95.69	15.36	10.00	6.65
C_6H_6	45.05	27.64	40.00	7.25

Table 4. Constants for Eq. (1).

The a_m and C values, as calculated by this procedure, were introduced into Eq. (1), in order to find by "trial and error" the values of g and n that give the best fit of experimental data. All the four characteristic parameters for each system were thus evaluated, and are reported in Table 4, while the very satisfactory agreement of experimental data with calculated adsorption curves is shown in Fig. 4.

As to a_m, the values reported in this work for two systems compare favourably with those that can be evaluated by a dielectric method, as it will be shown in a next paper. The corresponding data are reported in Table 5. Similarly, it is possible to evaluate the parameter n independently, through the knowledge of the mean pore radius according to KELVIN[7]. To this purpose the desorption branch of the hysteresis loop was employed. In Fig. 5 the pore size distribution functions are reported, which yield an identical r_K value of 15 Å for the three systems. By usual assumptions on molecular dimensions, n values were then calculated in substantial agreement with those resulting from Eq. (1) (Table 5).

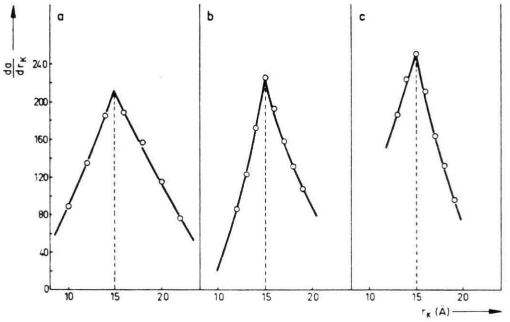

Fig. 5. KELVIN pore distribution function for γ-Al_2O_3: a = from C_6H_6 desorption; b = from CCl_4 desorption; c = from cyclo-C_6H_{12} desorption.

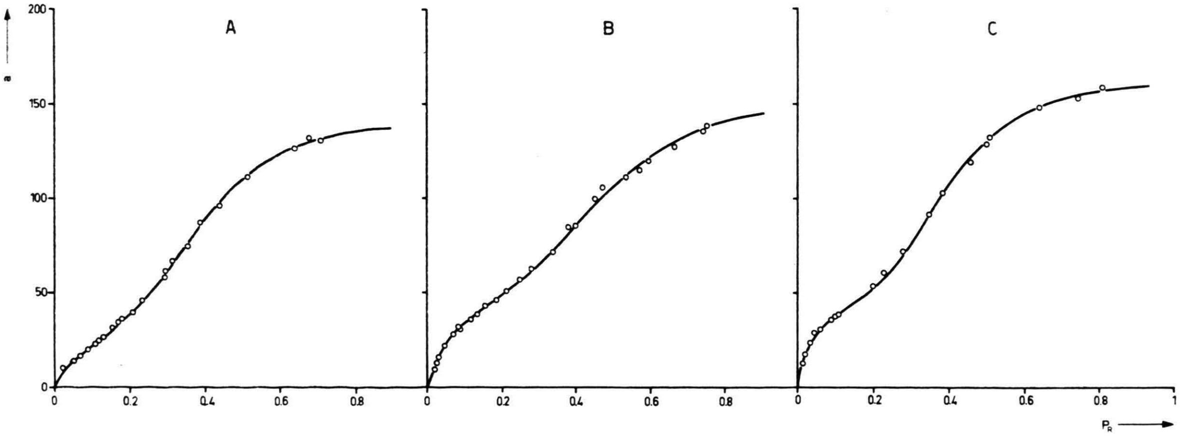

Fig. 4. Fitting of calculated adsorption isotherms to experimental data. A = cyclo-C_6H_{12}; B = CCl_4; C = C_6H_6. ——— calculated by Eq. (1), ○ experimental.

adsorbate	a_m(mg/g)		n	
	from Eq. (1)	from dielec. measurements	from Eq. (1)	from KELVIN radius
cyclohexane	43.98	—	6.50	7.11 *
carbon tetrachloride	95.69	96.5	6.65	6.53
benzene	45.05	40.2	7.25	7.90 *

* Calculated assuming the molecules as adsorbed flat in monolayer, randomly oriented in further layers.

Table 5. Comparison of a_m and n values.

From the g values of Table 4, values of Q were calculated which are of the same order as those evaluable from the Eötvös constant and the surface tension of the liquids according to CLAMPITT and GERMAN's procedure [6]. This latter method, however, leads to an "a priori" value for g, and the above authors stated that variations from this calculated value do not improve the fitting of data significantly. But in this work it was found that for at least two systems a substantial improvement of the fitting is achieved with rather large changes of g from the "surface tension values" (see Table 6). In one case only (CCl_4) both g values are in somewhat better accordance. Possibly the treatment of the cited authors is more satisfactory in the case of symmetrical molecules.

adsorbate	g from Eq. (1)	Q (kcal/mole) from g	Q_1 (kcal/mole) from surface tension	g_1 from Q_1
cyclohexane	25.00	1.91	1.64	16.03
carbon tetrachloride	10.00	1.36	1.55	13.78
benzene	40.00	2.19	1.63	15.71

Table 6. Comparison of g and Q values.

The C value (27.64) found in this work for the system $C_6H_6-\gamma\text{-}Al_2O_3$ is almost the same as that reported [2] for the system $C_6H_6-Fe_2O_3$ (27.0). From our C value, the energy $E_1 = 12.24$ kcal/mole is calculated: this is in good agreement with the mean interaction energy of the monolayer (~ 12.5 kcal/mole), as obtained from calorimetric measurements [14]. It should be noted that for this calculation, instead of the original definition for C [Eq. (2)], the relation [6] has been employed:

$$C = \exp\{(E_1 - E_L - Q)/RT\} . \qquad (4)$$

From CLAMPITT and GERMAN's definition for Q ($Q = E_L - E_S$, where E_S = heat of vaporization from a surface layer of the liquid) we might state that the B.D.D.T. "additional adsorption energy" can be identified with the work required to carry one mole of a liquid from the bulk to the surface layer, before evaporation.

For comparison, the quantity E_1 has been computed in three distinct ways: 1) by Eq. (4) with Q values of Table 6; 2) by Eq. (4) but with Q_1 values of the same table; and 3) by Eq. (2). These values are reported in the same order in Table 7. For the system $C_6H_6-\gamma\text{-}Al_2O_3$, the only one for which a comparison with calorimetric data is possible, the agreement is best with the value calculated by the first of the above procedures.

adsorbate	E_1 (calculated)			E_1 calorim.	E_L
	(1)	(2)	(3)		
cyclohexane	10.95	11.38	9.04	—	7.90[15]
carbon tetrachloride	10.82	11.02	9.46	—	7.84 *
benzene	12.24	11.69	10.06	12.5	8.09[15]

* From vapour pressure data at 20° and 30 °C [11].

Table 7. Average interaction energy (kcal/mole) at gas-solid interface.

From the values of column 1 (Table 7), it is seen that the mean interaction energy of the monolayer amounts to about 11 kcal/mole for both cyclohexane and carbon tetrachloride, and is higher than 12 kcal for benzene. The increase might be readily explained in terms of molecular structure, as shown in similar cases [16, 17].

In general, the substantial accordance of the four constants with independently derived values supports the opinion that Eq. (1), in spite of some drastic assumptions in its derivation, is able to describe type IV isotherms satisfactorily, by means of parameters of definite physical meaning.

The authors are greatly indebted to R. MONTEROSSO and F. DORPEMA of the C.E.T.I.S. (Ispra) for their helpful assistance with the IBM 7090 computer.

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