Gas-Solid Interaction

II: Dielectric Behaviour of Apolar Vapours Adsorbed on γ-alumina [*, **]

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The adsorption of vapours of C_6H_6, CCl_4 and cyclo-C_6H_{12} respectively on γ-Al_2O_3 is followed by means of electric capacity measurements, and the dielectric isotherms are drawn for the three heterogeneous systems. The shape of the isotherms is discussed, and equations are proposed for calculating the apparent dielectric constants of the adsorbates from the slopes of the isotherms.

In physical adsorption the interaction of adsorbed molecules with solids is mainly due to induction forces acting between the surface electric field and permanent or induced dipoles in the adsorbate, and to London dispersion forces, these prevailing, for example, in adsorption of apolar molecules [1].

In the last years it has been shown that the dielectric behaviour of the heterogeneous adsorbent-adsorbate systems is deeply affected by the predominant type of interaction; it became also apparent that, while dielectric data relating to polar adsorbed phases can generally be treated in terms of hindered or restricted rotation of dipoles close to the adsorbing surface, greater difficulties are involved when dealing with apolar adsorbed phases [2]. In the latter case, e. g. some characteristic discontinuities of dielectric isotherms have not been clearly and uniquely explained.

In this work the dielectric behaviour of cyclohexane, carbon tetrachloride and benzene, respectively, adsorbed on γ-alumina was experimentally investigated at 25 °C. The adsorption isotherms of these systems had been reported in a previous paper [3].

Experimental

Apparatus and materials. The apparatus, including vacuum pump and line, the thermostat and the pyrex container of the dielectric cell, was substantially the same as the one employed for previous adsorption measurements [3]. By simply interchanging the pyrex covers of the adsorption chamber, it was possible to introduce into the latter, instead of the bulb for gravimetric measurements, a capacitor-cell consisting of two coaxial gold-plated brass cylinders mounted on a stout teflon base and firmly held apart by teflon spacers. Electrical vacuum-tight connection was effected by two conical brass joints, exactly fitting into ground-glass sockets on the cover, corresponding to the condenser-cell terminals. Outside, the joints allowed the insertion of a standard General Radio Co. coaxial connector.

The measurements of electric capacitance and dissipation factor were made by means of a General Radio capacitance bridge type 716-CS1; variable frequency oscillator and null detector system also were from General Radio.

The geometric capacity of the cell was about 250 pF.

The materials used (cyclo-C_6H_{12}, CCl_4, C_6H_6 and γ-Al_2O_3) were identical to those previously employed and were treated by the same procedures [3].

Results. For each of the systems studied the capacity increments of the condenser-cell filled with the probe referred to the initial capacity due to Al_2O_3 alone, were measured as a function of the equilibrium pressure of the vapour phase. Isothermal measurements (25 °C) were extended over a frequency range from 0.1 to 1.4 Mc/sec, in order to reveal relaxation phenomena possibly occurring in that range. The very small tg δ values, however, showed no significant trend and

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3 M. Sanesi and V. Wagner, Z. Naturforschg. **22 a**, 203 [1967].
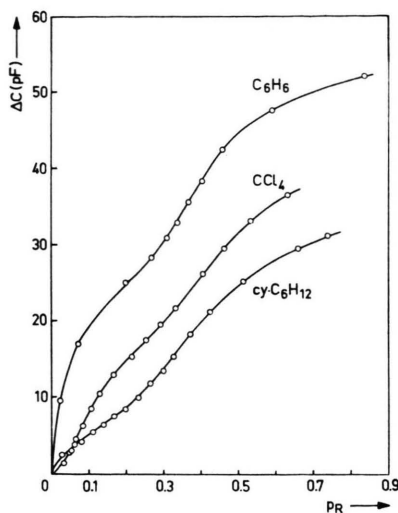

Fig. 1. Electric capacity increments at 1 Mc/sec, as a function
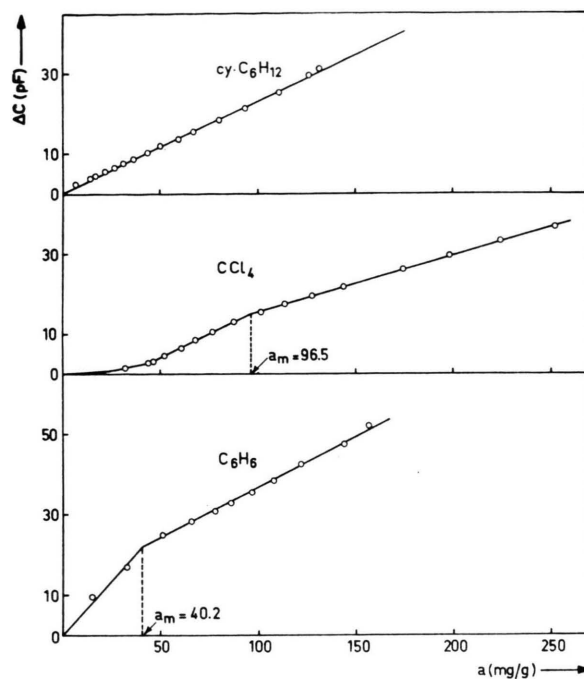of relative pressure.

Fig. 2. Dielectric isotherms on γ-alumina at 25 °C.   →

always remained approximately the same as with Al_2O_3 alone. They required no discussion and consequently were not reported in this paper.

In Fig. 1 the capacity increments ΔC at 1 Mc/sec are plotted vs. relative pressure $p_R = p/p_0$, where p_0 = vapour pressure of liquid at 25 °C.

From the adsorption isotherms at the same temperature [3] the amount adsorbed a was evaluated for each p_R value, thus allowing to draw dielectric isotherms (i. e., plots of ΔC vs. a). The experimental data are reported in Table 1, while the dielectric isotherms are shown in Fig. 2.

cyclo-hexane			carbon tetrachloride			benzene		
p_R	a mg/g	ΔC pF	p_R	a mg/g	ΔC pF	p_R	a mg/g	ΔC pF
0,0277	7,8	2,42	0,0307	32,0	1,37	0,0214	15,0	9,51
0,0625	14,8	3,85	0,0492	44,5	2,77	0,0693	32,3	16,95
0,0809	17,9	4,29	0,0527	46,7	2,99	0,1971	51,4	25,07
0,1107	22,7	5,47	0,0650	52,6	4,55	0,2664	66,0	28,33
0,1414	27,5	6,47	0,0843	61,0	6,32	0,3090	77,9	30,89
0,1681	31,9	7,51	0,1045	68,8	8,54	0,3356	86,5	32,90
0,1988	37,3	8,54	0,1299	77,1	10,43	0,3676	97,0	35,60
0,2326	44,1	10,02	0,1677	88,0	12,94	0,4049	108,1	38,32
0,2644	51,0	11,80	0,2151	101,9	15,40	0,4581	122,0	42,51
0,3003	60,2	13,47	0,2529	113,9	17,47	0,5902	144,1	47,62
0,3279	67,9	15,35	0,2932	128,0	19,54	0,8353	157,2	52,16
0,3740	80,8	18,22	0,3336	144,5	21,71			
0,4243	94,1	21,18	0,4065	175,1	26,15			
0,5134	111,6	25,32	0,4627	198,8	29,50			
0,6589	127,0	29,55	0,5338	225,0	33,16			
0,7399	132,4	31,23	0,6321	252,8	36,61			

Table 1. Electric capacity changes at 1 Mc/sec (25 °C).

Discussion

The curves in Fig. 1 are generally similar in shape to type IV isotherms, thus suggesting proportionality between ΔC and a. Actually (Fig. 2), for the system cyclo-$C_6H_{12} - \gamma$-Al_2O_3 the dielectric isotherm is given by a single straight-line; for the system with C_6H_6 there are two linear portions intersecting at $a = 40.2$ mg/g, and in the case of CCl_4 a linear relationship is obeyed for $a > 96.5$ mg/g. The occurrence of a discontinuity in the dielectric isotherm of C_6H_6 was first found by THORP [4], but not surely confirmed in later experiments by the same author [5]. He writes: "at such low sorptions the values of ΔC are very small, ... so little emphasis can be put on this break of the isotherm, although it does occur in the region of monolayer completion" [6]. In the present case, however, the use of a dielectric cell having a geometric capacity about ten times as large as that used by THORP, has enabled us to bring the phenomenon to evidence with certainty.

The simple relationship first suggested by ARGUE and MAASS [7]

$$\varepsilon = \sum_i \Phi_i \varepsilon_i, \qquad (1)$$

where ε = apparent dielectric constant of the heterogeneous system, ε_i = dielectric constant of i-th phase, Φ_i = volume fraction of the same phase, was repeatedly employed [8-10], although it was recognized by several authors [11, 12] to be of empirical nature only. Recently the usefulness of BRUGGEMANN's and BÖTTCHER's calculations [13] of dielectric constants of heterogeneous systems formed with crystalline powders and gases (or liquids) has been emphasized [14]. By an extension of these treatments to the systems studied in this work, these can be considered as consisting of two phases: the adsorbate and the solid with residual void space (thus neglecting the contribution to the polarization from the vapour); then BRUGGEMANN's and BÖTTCHER's equations can be written respectively as follows:

$$\frac{\varepsilon_a - \varepsilon}{\varepsilon_a - \varepsilon_s'} = (1 - \Phi_a) \sqrt[3]{\varepsilon/\varepsilon_s'}, \qquad (2)$$

$$\frac{\varepsilon - \varepsilon_s'}{3\,\varepsilon} = \Phi_a \left(\frac{\varepsilon_a - \varepsilon_s'}{\varepsilon_a + 2\,\varepsilon} \right), \qquad (3)$$

where ε = apparent dielectric constant of the heterogeneous system, ε_s' = apparent dielectric constant of the adsorbent, ε_a = dielectric constant of the adsorbate and Φ_a = fraction of total volume occupied by the adsorbate.

When $\varepsilon \cong \varepsilon_s'$, from Eq. (2) it follows

$$\varepsilon = \varepsilon_s' + \Phi_a(\varepsilon_a - \varepsilon_s'). \qquad (4)$$

In turn, Eq. (3) can conveniently be given the form

$$\varepsilon = \varepsilon_s' + \tfrac{3}{2}\,\Phi_a(\varepsilon_a - \varepsilon_s') + (\varepsilon_a/2)\,(\varepsilon_s'/\varepsilon - 1)$$

which, applying the same condition, reduces to

$$\varepsilon = \varepsilon_s' + \tfrac{3}{2}\,\Phi_a(\varepsilon_a - \varepsilon_s'). \qquad (5)$$

It can be noted that Eq. (4) is identical to Eq. (1) written for the two phases under consideration, while Eq. (5) differs from it by a factor $3/2$. For the present systems, as well as for all those in which the adsorbed phase is apolar and consequently has a low value of the dielectric constant, the approximation $\varepsilon = \varepsilon_s'$ is quite acceptable.

Both Eq. (4) and (5) account for linear dielectric isotherms, if dielectric constant and density of the adsorbed phase remain constant. A behaviour of this type is shown by cyclo-C_6H_{12}, no characteristic point being detectable in coincidence of monolayer completion. For the other two systems, however, the attainment of complete monomolecular surface coverage [3] is clearly indicated by the presence of breaks in the corresponding dielectric isotherms [2, 4]. (The a_m values shown in Fig. 2 are in good agreement with those obtained from adsorption isotherms [3]).

According to the very simplified description of Eq. (4) and (5), the abrupt change in slope might be caused, all other conditions being unchanged, by variations of the adsorbate density or of its dielectric constant or of the electric field acting on molecules before and after monolayer completion. Generally such effects might be concurrent.

The assumption of a density change, which had already been shown not valid in other cases [15], can

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be considered as furthermore disproved by the present results, especially on account of the striking difference existing between the isotherms for cyclo-C_6H_{12} and the other two. On the same ground, it seems possible to exclude that the effect might be mainly due to changes of the electric field. This latter hypothesis had been put forth principally because discontinuities in dielectric isotherms had been previously observed only with apolar vapours adsorbed on *porous* solids, while straight-line isotherms with no discontinuties had been obtained with *non-porous* adsorbents (e. g., butane on rutile [16]).

The starting portion of the CCl_4 dielectric isotherm, markedly differing from that of the other two, might be considered as an interesting indication of a "stepwise adsorption" [17] taking place at very low surface coverages, which could not be sufficiently revealed by the "classic" adsorption isotherm [3] because of the experimental conditions. It appears worth studying this particular point more deeply.

Finally, Eq. (4) and (5) have been employed to calculate the dielectric constants of adsorbate, over the capillary condensation range, after transformation into the more convenient forms

$$\varepsilon_a - \varepsilon_s{}' = \frac{\partial \Delta C}{\partial a} \cdot \frac{1000 \, d_L}{C_0 \, d_s{}'} \qquad (6)$$

and

$$\varepsilon_a - \varepsilon_s{}' = \frac{2}{3} \frac{\partial \Delta C}{\partial a} \cdot \frac{1000 \, d_L}{C_0 \, d_s{}'}, \qquad (7)$$

where a is expressed in mg/g; $d_s{}' = $ apparent density of adsorbent (for the Al_2O_3 sample employed, $d_s{}' = 1.008$); $d_L = $ density of adsorbate as a liquid; $C_0 = $ geometric capacity of the condenser-cell. The results are reported in Table 2, where α denotes the value of the slope $\partial \Delta C / \partial a$ calculated by the least square method; for comparison, the dielectric con-

adsorbate	α	$d_L{}^{20}$	ε_a calc.		$\varepsilon_L{}^{21}$
			Eq. (6)	Eq. (7)	
cyclo-hexane	0,2257	0,774	2,80	2,55	2,015
carbon tetrachloride	0,1405	1,585	2,96	2,66	2,228
benzene	0,2252	0,874	2,90	2,62	2,274

Table 2. Dielectric constants of the adsorbate at 25 °C.

stants of the corresponding liquids and the literature d_L values used in the calculation are also reported in the table. It is seen that ε_a values obtained by Eq. (6) deviate more from those of the liquid state than those calculated by Eq. (7). The latter seems therefore preferable. The fact that the calculated values are higher than those for the liquids might be due, on one hand, to the adsorbate density being lower than that of the corresponding liquid (as reported in other cases [18, 19]); and on the other hand to the contribution (at least in the case of C_6H_6 and CCl_4) of induced dipole moments.

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