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ADSORPTION ISOTHERMS OF HYDROCARBONS ON γ-ALUMINA

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SUMMARY

Adsorption isotherms on γ-alumina of hydrocarbons with up to eight carbon-atoms were investigated using the gas chromatographic method of Cremer and Huber[1]. Under suitable conditions of flow-rate and amount of substances there was scarcely any peak broadening by diffusion. The experimental isotherms could be fitted using either the Langmuir or the Freundlich relation. Values for the constants are tabulated for temperatures between 473 and 643 °K. Heats of adsorption were directly evaluated for different C_6 compounds. Increments for an approximate calculation of adsorption isotherms were calculated from the experimental values.

INTRODUCTION

The great importance of alumina as an active catalyst support, especially for petrochemical reactions, makes it necessary to investigate the adsorption of hydrocarbons on the catalyst as well as on the support. Knowledge of these adsorption isotherms at higher temperatures may for instance greatly improve calculations of kinetic models[2]. Cremer and Huber[1] described a gas chromatographic (GC) method to determine adsorption isotherms from the shape of peaks obtained with an adsorption column. From a simplified mass balance equation they obtained:

$$\frac{dn}{dc} = \frac{V_c}{m} \tag{1}$$

or after integration

$$n = \frac{1}{m}\int_0^c V_c \, dc \tag{2}$$

where

n = amount of adsorbed substance (mole/g)
m = mass of adsorbant (g)
V_c = retention volume (ml)
c = concentration in the gas phase (mole/ml)

The equations did not take into account peak broadening by diffusion. Several empirical methods for corrections have been described[3–7], but they are theoretically not well founded and give different results.

Previous investigations of the adsorption of hydrocarbons on alumina described in the literature[8–14] either were only partially concerned with chromatographic aspects, or else only a few hydrocarbons were studied.

EXPERIMENTAL

A Perkin-Elmer Model 900 gas chromatograph was used, fitted with a 65 cm × 0.25 in. I.D. stainless steel column filled with γ-alumina (particle size 140–200 μm) (Tonerde reinst, E. Merck, Darmstadt, G.F.R.). The alumina samples were heated to 500 ± 5 °C for 2 h before the experiments using a newly constructed oven, which could be used in the chromatograph.

Measurements were made at 200, 250, 300 and 370 °C. The alumina samples had a specific surface area of 82.6 ± 1.0 m^2/g (B.E.T.). The hydrogen used as carrier gas was passed over P_2O_5 and through an adsorption trap filled with molecular sieve and cooled with liquid nitrogen. The hydrocarbons used were the purest obtainable. The liquids were dried using freshly heated molecular sieve. A heat-conduction detector was used, which permitted the determination of the dead time using helium.

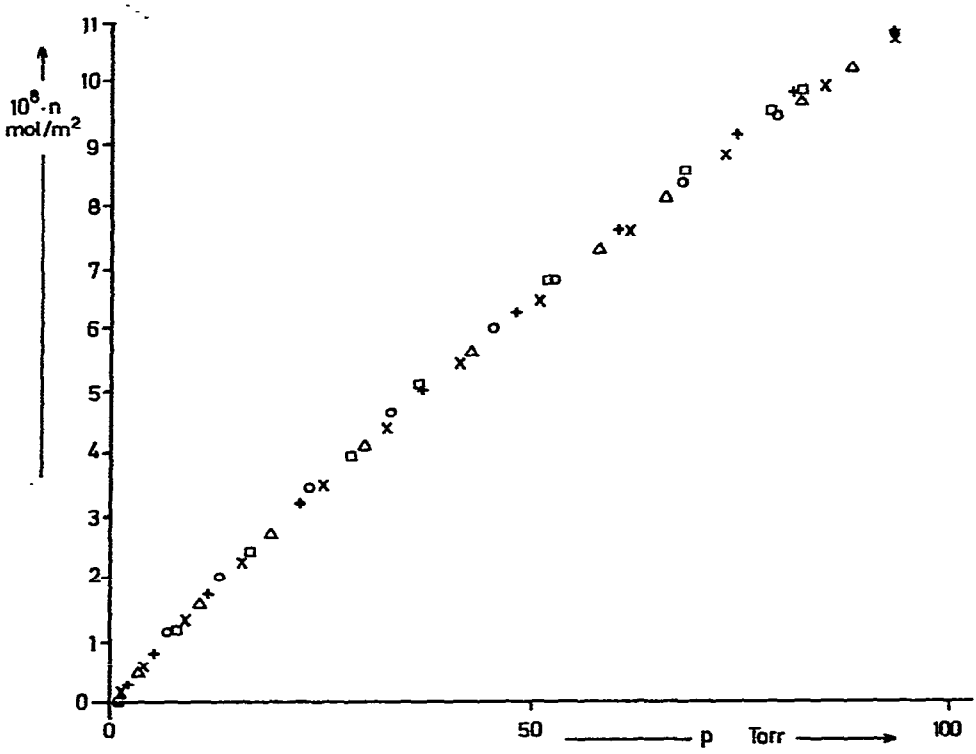

Fig. 1. Reproducibilities of adsorption isotherms of hexane on Al_2O_3 at 473 °K using different carrier gas velocities. ○, 5.8 ml/min; ×, 15.6 ml/min; +, 20.0 ml/min; △, 25.6 ml/min; □, 44.0 ml/min.

Dead time, time of the maxima and peak areas were determined with an integrator (Autolab System IV), and eqn. 2 was evaluated with a small computer (Model HP 9830 A, Hewlett-Packard).

RESULTS AND DISCUSSION

The dependence of the calculated isotherms on carrier gas velocity was investigated. Fig. 1 shows that only at very low velocities there is a very small deviation. This deviation may be the result of peak broadening by diffusion. From the other curves one may conclude that it should not be necessary to use diffusion corrections under the given conditions. For subsequent experiments the carrier gas velocities used were between 10 and 40 ml/min. Thus the results shown in Fig. 1 may be taken as proof of the good reproducibility of the method.

After a few preliminary calculations, which showed that neither Henry nor Temkin isotherms could be used, non-linear regression calculations were made for all substances and temperatures to fit the experimental results with either Langmuir [$n = ap/(b + p)$] or Freundlich ($n = a' p^{b'}$) type isotherms (a, b, a' and b' are constants, p is partial pressure of hydrocarbon.) Fig. 2 shows the results obtained for hexane at 473 °K. The experimental values are best fitted by a Langmuir isotherm. The mean value of the standard deviations of the measured points from the calculated curves is $2.3 \cdot 10^{-10}$ mole/m² for the Langmuir isotherms and $5.0 \cdot 10^{-10}$ mole/m² for Freundlich isotherms, *i.e.* both types of isotherm give deviations of less than 1%.

The constants of the isotherms for all substances and temperatures investigated

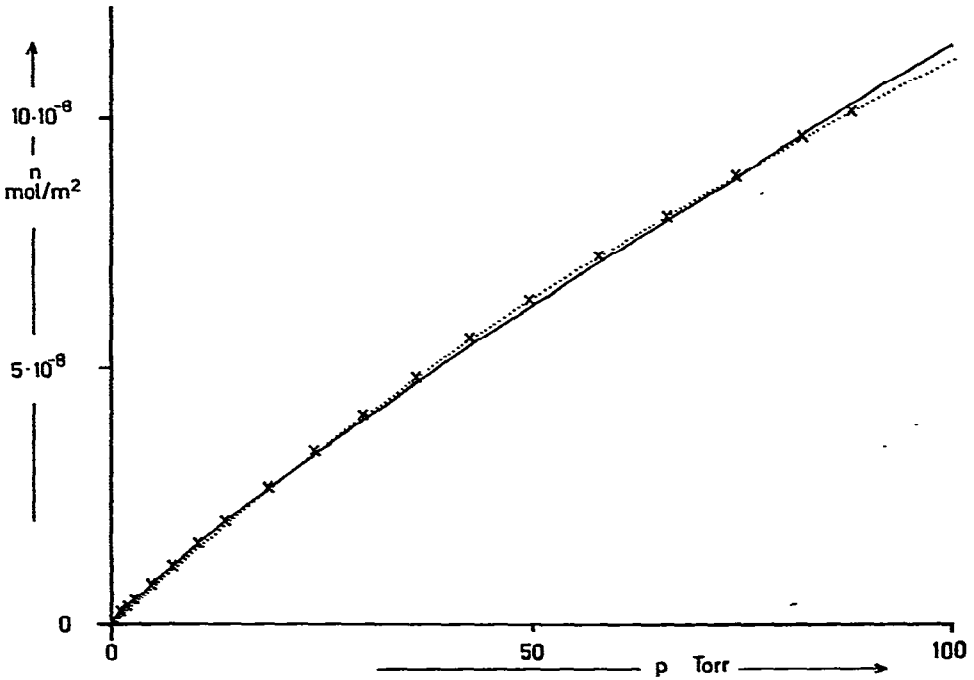

Fig. 2. Adsorption isotherms for hexane on Al_2O_3 at 473 °K. ×, Experimental values; ———, Freundlich isotherm (calculated); ·····, Langmuir isotherm (calculated).

TABLE I

CONSTANTS OF ADSORPTION ISOTHERMS

The adsorption constants for p in mmHg and n in mole hydrocarbon per m^2 Al_2O_3 surface.

Substance	*T (°K)*	*Langmuir*		*Freundlich*	
		$10^8 \cdot a$	b	$10^{10} \cdot a'$	b'
Methane	473	3.12	288.4	3.81	0.6030
Ethane	473	3.90	269.6	4.92	0.5947
Ethene	473	5.41	318.0	5.16	0.6428
Propane	473	8.21	356.5	5.91	0.6993
Propene	473	11.25	359.2	7.13	0.7374
Butane	473	15.68	412.2	7.46	0.7815
But-1-ene	473	21.79	393.0	9.50	0.8290
But-2-ene (*cis* + *trans*)	643	4.01	309.5	3.05	0.7290
cis-But-2-ene	473	23.04	391.6	9.95	0.8320
trans-But-2-ene	473	19.87	351.5	10.68	0.8015
Methylpropane	473	14.65	411.5	7.20	0.7746
Methylpropene	473	16.44	236.1	13.98	0.7648
Methylpropene	643	4.17	324.8	3.01	0.7364
Pentane	473	27.52	328.4	14.11	0.8256
Pentane	643	5.85	293.5	4.12	0.7595
Pent-1-ene	473	32.75	280.3	19.39	0.8222
Pent-1-ene	643	6.81	295.4	5.10	0.7392
cis-Pent-2-ene	473	32.69	275.8	19.60	0.8225
cis-Pent-2-ene	643	6.45	286.0	4.91	0.7395
trans-Pent-2-ene	473	33.09	280.8	19.54	0.8226
trans-Pent-2-ene	643	6.40	293.0	4.72	0.7450
Methylbutane	473	26.64	366.5	11.97	0.8173
Methylbutane	643	6.12	310.4	4.25	0.7507
2-Methylbut-1-ene	473	24.99	168.5	26.24	0.7766
2-Methylbut-1-ene	643	6.86	293.6	4.95	0.7479
2-Methylbut-2-ene	473	21.45	140.1	24.54	0.7934
2-Methylbut-2-ene	643	6.84	288.0	5.11	0.7425
3-Methylbut-1-ene	473	23.54	259.6	15.37	0.8126
3-Methylbut-1-ene	643	5.43	362.2	3.27	0.7592
Dimethylpropane	473	20.23	398.6	9.17	0.7971
Dimethylpropane	643	4.37	345.2	2.93	0.7391
Cyclopentane	643	6.10	290.2	5.01	0.7178
Cyclopentane	473	26.79	337.6	14.84	0.8018
Cyclopentene	473	40.44	380.6	18.15	0.8289
Cyclopentene	643	6.10	297.5	5.11	0.7429
Hexane	473	42.51	284.5	21.15	0.8653
Hexane	523	22.61	347.3	11.66	0.8134
Hexane	573	11.12	310.9	7.14	0.7815
Hexane	643	6.60	286.1	4.40	0.7775
Hex-1-ene	473	42.82	204.7	29.45	0.8534
Hex-1-ene	523	23.56	265.7	15.52	0.8060
Hex-1-ene	573	13.51	312.5	8.41	0.7884
Hex-1-ene	643	7.91	295.5	5.08	0.7796
Hex-2-ene (*cis* + *trans*)	473	43.23	204.3	29.77	0.8534
Hex-2-ene (*cis* + *trans*)	643	8.08	301.4	5.13	0.7792
2-Methylpentane	473	38.46	295.9	18.97	0.8584
2-Methylpentane	643	6.90	302.8	4.40	0.7778
3-Methylpentane	473	39.57	300.6	19.36	0.8567
3-Methylpentane	523	22.16	361.4	11.19	0.8108

TABLE I (*continued*)

Substance	*T* (°K)	*Langmuir*		*Freundlich*	
		$10^8 \cdot a$	*b*	$10^{10} \cdot a'$	*b'*
3-Methylpentane	573	11.11	312.4	7.37	0.7731
3-Methylpentane	643	7.03	305.5	4.38	0.7814
2,2-Dimethylbutane	473	35.06	300.1	17.59	0.8504
2,2-Dimethylbutane	643	6.69	295.2	4.36	0.7775
2,3-Dimethylbutane	473	37.69	297.6	18.78	0.8542
2,3-Dimethylbutane	523	20.54	342.6	11.17	0.8033
2,3-Dimethylbutane	573	10.71	309.3	7.18	0.7726
2,3-Dimethylbutane	643	6.89	297.6	4.40	0.7815
2,3-Dimethylbut-2-ene	473	37.85	181.4	30.69	0.8342
2,3-Dimethylbut-2-ene	523	18.94	190.0	18.36	0.7733
2,3-Dimethylbut-2-ene	573	13.31	305.9	8.62	0.7827
2,3-Dimethylbut-2-ene	643	7.75	279.6	5.33	0.7713
Methylcyclopentane	473	38.81	310.9	19.23	0.8462
Methylcyclopentane	523	21.04	341.7	11.85	0.7956
Methylcyclopentane	573	11.14	311.9	7.47	0.7548
Methylcyclopentane	643	7.33	300.0	4.93	0.7637
Cyclohexane	473	42.73	333.1	19.76	0.8489
Cyclohexane	523	22.47	350.0	12.10	0.8016
Cyclohexane	573	11.76	324.9	7.27	0.7626
Cyclohexane	643	7.72	313.6	5.04	0.7616
Cyclohexene	473	41.69	180.0	34.23	0.8324
Cyclohexene	523	24.74	244.0	18.25	0.7943
Cyclohexene	573	15.47	322.9	9.08	0.7795
Cyclohexene	643	8.95	299.0	5.84	0.7707
Benzene	473	47.10	110.4	59.16	0.8269
Benzene	523	34.99	244.2	23.51	0.8192
Benzene	573	21.34	337.8	11.18	0.7936
Benzene	643	11.83	333.0	6.74	0.7802
Heptane	473	50.94	189.9	34.75	0.8759
Heptane	643	9.26	316.8	4.85	0.8197
Hept-1-ene	473	45.56	113.8	50.48	0.8617
Octane	473	45.34	847.3	62.96	0.8740
Octane	643	11.16	299.9	5.62	0.8497
Oct-1-ene	643	13.30	321.7	6.35	0.8480
Oct-2-ene (*cis* + *trans*)	643	12.82	310.4	6.43	0.8431

are in Table I. Because the constant $1/b$ in a Langmuir isotherm should be the equilibrium constant for the adsorption process, only this value should be temperature dependent. The fact that it is almost independent of temperature, according to the experimental results, shows that the Langmuir formula, though it gives good correlations, cannot have great physical significance.

For some C_6 hydrocarbons the isotherms were determined at four different temperatures, hence it was possible to calculate isosteric heats of adsorption, q_{st} (kJ/mole). The results (R = gas constant)

$$q_{st} = -R \left(\frac{\partial \ln p}{\partial (1/T)} \right)_n \tag{3}$$

are in Table II. The values for benzene and hexane are in fairly good agreement with the results of Cremer and Huber[1]. For the Freundlich as well as for the Langmuir

TABLE II

ISOSTERIC HEATS OF ADSORPTION IN KILOJOULES PER MOLE

Substance	$10^8 \cdot n$ *(mole/m²)*	*Temperature interval (°K)*		
		473–523	*523–573*	*573–643*
Hexane	1.82	36.0	36.0	25.1
	3.03	37.7	38.5	—
	4.24	38.5	42.3	—
Hex-1-ene	1.82	37.7	40.2	26.4
	3.03	38.9	41.4	—
	4.24	39.8	43.5	—
Cyclohexane	1.82	31.0	33.5	21.8
	3.03	31.8	36.0	16.7
	4.24	32.2	39.4	—
Cyclohexene	1.82	36.4	41.9	25.5
	3.03	36.8	41.9	28.5
	4.24	37.7	43.1	—
Benzene	1.82	46.5	43.5	29.3
	3.03	46.5	44.4	31.8
	4.24	46.5	45.6	34.3

isotherms attempts were made to calculate the constants for non-cyclic compounds from increments. The optimization method of Nelder and Mead[15] was used to find the best values for the increments. The approximations were nearly the same with a Langmuir or a Freundlich isotherm. Standard deviations for the relative precisions ($[n_{obs} - n_{calc}]/n_{calc}$) were *ca.* 22%.

Langmuir

$$n = \frac{10^{a+b/T} \cdot p}{10^c + p} \tag{4}$$

where

$$a = -10.725 + 0.1902n_c + 0.0968n_d + 0.0184n_b$$
$$b = 1377.3 + 3.455n_c - 0.305n_d - 0.599n_b$$
$$c = 2.256 + 0.00138n_c - 0.0601n_d - 0.0165n_b$$

n_c = number of carbon atoms in hydrocarbon
n_d = number of double bonds in hydrocarbon
n_b = number of branchings in hydrocarbon

Freundlich

$$n = 10^{a+b/T} \cdot p^c \tag{5}$$

where

$$a = -12.915 + 0.2055n_c + 0.1532n_d + 0.00062n_b$$
$$b = 1354.9 - 2.867n_c + 0.0999n_d + 0.7361n_b$$
$$c = 0.8528 + 0.0033n_c - 0.0188n_d + 0.0109n_b$$

A Langmuir isotherm containing the temperature function in the denominator

$$n = \frac{10^{a} \cdot p}{10^{b+c/T} + p} \tag{6}$$

where

$$a = -7.949 + 0.1919n_c + 0.1176n_d + 0.0384n_b$$
$$b = 5.3486 + 0.00226n_c - 0.0148n_d + 0.0296n_b$$
$$c = 1551.19 + 1.1216n_c - 0.7392n_d + 0.6245n_b$$

as should be expected theoretically, had a standard deviation of 24%.

By combining eqn. 3 with eqn. 4, 5 or 6, values for the isosteric heat of adsorption using hexane were obtained, as follows:

From eqn. 4

$$q_{st} = \frac{2.3026\ R\ b}{1 - (n/10^{a+b/T})}$$

$$q_{st}(\text{hexane}) = 30.7 \text{ kJ/mole (for } n = 2.5 \cdot 10^{-6} \text{ mole/g)}$$

From eqn. 6

$$q_{st} = 2.3026 \cdot R \cdot c$$

$$q_{st}(\text{hexane}) = 29.7 \text{ kJ/mole}$$

From eqn. 5

$$q_{st} = 2.3026 \cdot R \cdot \frac{b}{c}$$

$$q_{st}(\text{hexane}) = 29.3 \text{ kJ/mole}$$

These values are in the range of values of Table II (25.1–42.3 kJ/mole for hexane).

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