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Adsorption of Butane, 2-Methylpropane, and 1-Butene on Activated Carbon

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Four adsorption isotherms at 278, 288, 293, and 303 K of butane, 2-methylpropane, and 1-butene are obtained on activated carbon. The results at pressures up to $0.8P/P_s$ are measured on an automated apparatus and correlated by the vacancy solution model of Cochran and Danner [*AIChE J.* **1985,** *31* (2), 268–277].

Introduction

The present study is devoted to the measurement of adsorption of butane, 2-methylpropane and 1-butene on activated carbon. In the literature, one may find measurements for butane on activated carbon up to 0.8 of the relative pressure and at several temperatures (*1*), but 2-methylpropane and 1-butene have been studied on activated carbon only at 298 K and at their boiling point up to 101 kPa (*2, 3*).

This work aims at determining the influence of a double bond and a branched structure on the adsorption capacity. For their industrial separation by an adsorption process, it is important to have equilibrium data on the same adsorbent and at different temperatures.

These measurements are the first in a series of studies on binary mixtures of linear or branched, saturated or unsaturated hydrocarbons over a wide range of pressure.

Experimental Section

The adsorbent used in this study is type F30/470 AC supplied by Chemviron Carbon. The surface area is 1100 $m^2\ g^{-1}$. The butane, 2-methylpropane, and 1-butene were obtained from Air Liquide Belgium with purities of 99.5, 99.5, and 99 vol %, respectively.

The automated apparatus is of the static volumetric type (*5*). It allows pure gas isotherms to be determined from 273 to 373 K and to pressures of 4000 kPa. In the method, the total quantity of gas admitted to the system and the amount of gas in the vapor phase remaining after adsorption equilibrium are determined by appropriate P–T–V measurements.

A schematic diagram of the apparatus is shown in Figure 1. The adsorption apparatus is maintained in a refrigerated incubator (I) regulated in temperature to within ±0.1 K. A computer fitted with a data acquisition card allows the control of the electrovalves (E1 and E2), the acquisition and the storage of the results. The main part of the apparatus consists of two vessels made from stainless steel, A and B. B is a buffer volume, and A is the adsorber. Both volumes are linked by an electrovalve (E2) and are designed to operate up to 4000 kPa. A heating wire (R) allows the adsorbent sample (S) to be regenerated "in situ". Pressure measurements are made by an Endress Hauser (Cerabar) absolute pressure transducer (P) coupled with its control card. Its pressure range is from 400 to 4000 kPa, and its accuracy is about ±0.1% of the scale. Temperatures in both volumes are measured using a Pt100 (T) (with an accuracy of ±0.1 K). The two electrovalves (one between A and B, the other at the gas inlet), the manual valves, and the tubes are made from stainless steel.

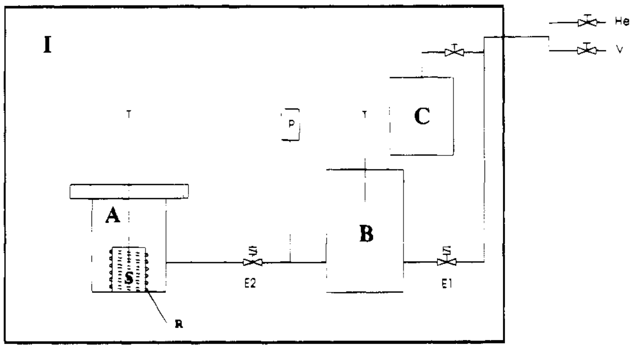

Figure 1. Experimental apparatus: (A) adsorber; (B) buffer tank; (C) gas reservoir; (E1, E2) electrovalves; (He) inlet inert gas; (P) pressure transducer; (R) heating wire; (S) adsorbent sample; (T) Pt100; (V) to the vacuum pump.

Table 1. Critical Temperature (T_c), Critical Pressure (P_c), and Acentric Factor (ω) of Butane, 2-Methylpropane, and 1-Butene

	T_c/K	P_c/kPa	ω
butane	425.2	3800	0.193
2-methylpropane	408.1	3650	0.176
1-butene	419.6	4020	0.187

Initially, the adsorbent is treated to eliminate any trace of pollutants by heating at 423 K during a 24 h period in a drying oven. It is then weighed (about 20 g with an accuracy of ±0.1 mg) and introduced into the adsorber. The volume of A is measured for each new sample of adsorbent by successive expansions of helium which is considered as an inert gas. The operating procedure for pure-gas isotherm determinations is to admit the gas into the buffer volume (B), to measure its temperature and pressure, to expand the gas into the adsorber (A), and finally to record the equilibrium temperature and pressure. This equilibrium adsorption is attained when the pressure is constant at 0.5 kPa for 25 min.

The knowledge of temperature, pressure and gaseous volume before and after each adsorption step leads to the mole number of gas before and after adsorption and finally, by difference, to the adsorbed quantity. The calculation of the gaseous mole numbers is performed using the Redlich–Kwong equation of state (*4*). The parameters of butane, 2-methylpropane, and 1-butene used in the Redlich–Kwong equation are given in Table 1.

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Table 2. Adsorption Isotherms for Butane on F30/470 Activated Carbon at 278 and 288 K

T/K = 278, P_s/kPa = 123.7		T/K = 288, P_s/kPa = 175.53	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
1.42	1.43	1.71	1.57
1.66	1.52	1.83	1.66
1.79	1.62	2.08	1.75
2.03	1.76	2.32	1.94
2.16	1.91	2.45	2.13
2.65	2.09	3.31	2.30
2.90	2.33	3.81	2.48
3.27	2.60	5.29	2.72
4.75	2.91	8.01	2.94
10.19	3.26	12.46	3.13
21.12	3.54	21.85	3.31
29.10	3.60	35.67	3.47
71.87	3.90	58.19	3.61
		85.26	3.76
		127.16	3.95

Table 3. Adsorption Isotherms for Butane on F30/470 Activated Carbon at 293 and 303 K

T/K = 293, P_s/kPa = 207.01		T/K = 303, P_s/kPa = 282.7	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
1.48	1.50	1.53	1.31
1.73	1.69	1.56	1.52
2.10	1.89	2.40	2.06
2.60	2.08	6.84	2.65
2.97	2.28	12.41	2.91
3.21	2.48	31.19	3.23
5.07	2.66	47.51	3.32
8.16	2.90	74.21	3.48
13.47	3.11	121.67	3.64
25.09	3.29	159.12	3.73
39.18	3.41	185.69	3.82
56.98	3.53	193.85	3.85
80.22	3.65	201.02	3.88
110.13	3.77	212.34	3.92
153.76	3.96	236.86	4.14

Table 4. Adsorption Isotherms for 2-Methylpropane on F30/470 Activated Carbon at 278 and 288 K

T/K = 278, P_s/kPa = 187.03		T/K = 288, P_s/kPa = 260.01	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
2.70	1.25	0.63	1.68
2.82	1.45	0.59	1.88
3.19	1.65	1.21	2.08
3.93	1.83	2.08	2.29
3.95	2.05	3.56	2.48
4.30	2.24	8.01	2.73
4.79	2.40	15.67	2.91
6.03	2.56	26.55	3.04
7.27	2.73	42.74	3.16
8.75	2.87	59.30	3.25
11.59	3.01	79.08	3.33
18.76	3.22	102.69	3.42
28.77	3.36	129.26	3.51
39.03	3.46	161.40	3.62
50.40	3.54	206.26	3.82
61.40	3.62		
76.73	3.70		
93.66	3.78		
113.69	3.88		
142.98	4.02		

Results and Discussion

Equilibrium Results. Adsorption isotherms for butane, 2-methylpropane, and 1-butene on activated carbon at 278, 288, 293, and 303 K are obtained at relative pressures up to 0.8. The experimental equilibrium results are presented in Tables 2–7. Several sets of measurements are reproduced with differences less than 1%. The results for 2-methylpropane and 1-butene on F30/470 activated carbon at 303 K are shown in Figure 2.

Table 5. Adsorption Isotherms for 2-Methylpropane on F30/470 Activated Carbon at 293 and 303 K

T/K = 293, P_s/kPa = 303.66		T/K = 303, P_s/kPa = 407.04	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
0.25	1.57	3.63	0.68
0.74	1.79	4.77	1.00
0.87	2.01	5.98	1.33
2.10	2.22	6.84	1.62
3.21	2.42	11.17	2.40
5.56	2.59	28.35	2.86
13.84	2.84	57.27	3.08
25.34	3.00	71.12	3.14
38.93	3.11	113.02	3.27
54.26	3.19	142.56	3.34
69.34	3.25	159.37	3.38
84.42	3.32	186.56	3.44
105.93	3.39	210.41	3.50
125.70	3.45	223.14	3.55
149.31	3.52	250.34	3.64
180.65	3.60	258.87	3.72
206.04	3.70	283.71	3.99
246.46	3.90	316.71	4.22

Table 6. Adsorption Isotherms for 1-Butene on F30/470 Activated Carbon at 278 and 288 K

T/K = 278, P_s/kPa = 153.4		T/K = 288, P_s/kPa = 215.6	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
0.50	1.55	1.83	1.59
0.52	1.69	2.08	1.73
0.53	1.82	2.09	1.89
0.55	1.94	2.32	2.04
0.56	2.07	2.69	2.27
0.80	2.25	3.31	2.49
1.05	2.43	3.81	2.71
1.42	2.66	5.78	2.99
1.91	2.95	9.25	3.24
4.14	3.26	17.03	3.49
9.33	3.57	31.25	3.68
22.68	3.88	50.28	3.84
50.61	4.13	76.82	3.99
101.16	4.41	110.97	4.15
		161.52	4.37

Table 7. Adsorption Isotherms for 1-Butene on F30/470 Activated Carbon at 293 and 303 K

T/K = 293, P_s/kPa = 253.1		T/K = 303, P_s/kPa = 342.8	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
0.86	1.50	0.29	1.16
0.88	1.69	0.66	1.33
1.24	1.87	0.91	1.69
1.48	2.06	2.77	2.44
1.73	2.25	10.92	3.09
2.35	2.51	33.42	3.49
3.83	2.77	65.55	3.70
6.18	3.02	101.52	3.84
10.26	3.25	138.23	3.95
19.53	3.48	173.58	4.06
33.00	3.65	207.82	4.16
52.90	3.80	238.59	4.28
77.00	3.93	267.15	4.40
106.17	4.04	286.30	4.62
141.84	4.19		
194.55	4.39		

The curves are similar in shape and have a classic isotherm form.

The adsorbed gases are formed by molecules containing the same number of carbon atoms but having different degrees of unsaturation and branching. The vapor pressures (P_s) of the three compounds are similar, so the effect of the differences in structure is the major factor. For the same relative pressure (P/P_s), the amount adsorbed on activated carbon increases with the presence of a double bond and decreases for the branched compound as shown in Figure 3.

Table 8. Temperature-Independent Regression Parameters for the Flory–Huggins Form of the Vacancy Solution Model on F30/470 Activated Carbon up to 0.55P/P_s

adsorbate	N_{01}^{∞}/(mol·kg^{-1})	r_1/K	$b_{01} \times 10^6$ (mol·kg^{-1}·kPa^{-1})	$-q_1 \times 10^{-4}$ (J·mol^{-1})	$m_1 \times 10^{-3}$ (kg·mol^{-1})	no. of exptl results up to 0.55P/P_s	std dev in pressure/kPa
butane	4.788	25.9	7.35	2.999	0.94	52	3.22
2-methylpropane	1.9808	251.25	164.52	2.145	11.41	55	6.15
1-butene	5.0782	24.9	0.80	3.602	0.84	50	2.86

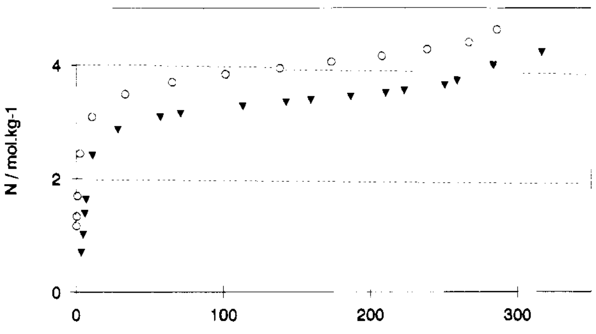

Figure 2. Adsorption results for 2-methylpropane and 1-butene on F30/470 activated carbon at 303 K: ▼, 2-methylpropane; ○, 1-butene.

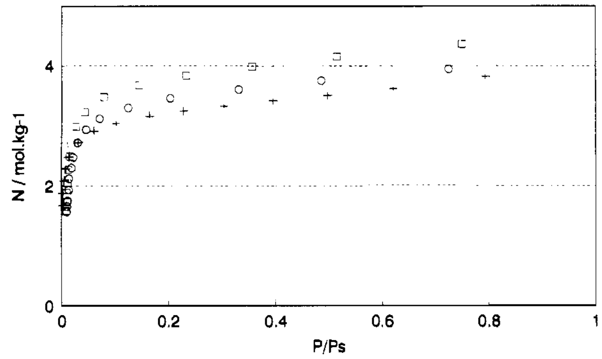

Figure 3. Adsorption results for butane, 2-methylpropane, and 1-butene on F30/470 activated carbon at 288 K: ○, butane; +, 2-methylpropane; □, 1-butene.

Correlation. The correlation of the results has two aims. The first one is to obtain physical parameters of a model for the correlation of isotherms over a wide range of pressures and at different temperatures. Secondly, this model must also be able to predict from pure-gas parameters the behavior of multicomponent adsorption on the same media, without any modification. There are few models performing these requirements.

Previous studies (*7*) have indicated that the vacancy solution is a successful model. This approach is based on solution thermodynamic concepts. The adsorption isotherm equation of the Flory–Huggins form of the vacancy solution model (VSM-FH) is

$$P = \left(\frac{N_1^{\infty}}{b_1}\frac{\theta}{1-\theta}\right)\exp\left(\frac{\alpha_{1v}^{2}\theta}{1+\alpha_{1v}\theta}\right) \tag{1}$$

In the vacancy solution model, θ is the coverage factor and is defined by

$$\theta = N/N_1^{\infty} \tag{2}$$

where N and N_1^{∞} are the adsorbed amount and the maximum adsorbed amount of pure component, respectively.

In eq 1, the material within the first set of parentheses is in the form of the well-known Langmuir equation. The exponential term is a correction which depends on the activity coefficient given by Flory–Huggins. In this equation, the Henry's law constant, b_1, and the isosteric heat of adsorption at infinite dilution, q_1, are related theoretically by the following expression

$$b_1 = b_{01}\exp(-q_1/RT) \tag{3}$$

The parameter b_{01} characterizes the adsorbate–adsorbent system and is independent of temperature.

An empirical equation (4) was used to describe the temperature dependence of the maximum adsorbed amount of pure component, N_1^{∞}

$$N_1^{\infty} = N_{01}^{\infty}\exp(r_1/T) \tag{4}$$

α_{1v} is the parameter describing nonideality in the adsorbed phase induced by interaction between the pure component and the vacancy. Its temperature dependence was also determined empirically. A direct correspondence in many systems between α_{1v} and N_1^{∞} is observed and may be expressed by the following equation:

$$\alpha_{1v} = m_1 N_1^{\infty} - 1 \tag{5}$$

where the constant m_1 is assumed to be independent of temperature.

Cochran et al. have shown that, if a number of isotherms are available for pure gas, instead of regressing three parameters for each temperature (N_1^{∞}, b_1, and α_{1v}), all data should be used simultaneously to obtain the five parameters (N_{01}^{∞}, r_1, b_{01}, q_1, and m_1). This approach will allow excellent interpolation within, and reasonable extrapolation outside of, the experimental temperature range. Furthermore, the parameters so determined are more consistent and have been found to give better binary and ternary mixture predictions than parameters determined from only isothermal data (*7*).

The values of temperature-independent regression parameters for the VSM-FH are listed in Table 8. The Flory–Huggins form of the vacancy solution model gives good results up to 0.55 P/P_s. The obtained results give parameters with a physical signifiance. At all temperature, the maximum adsorbed amount per mass of adsorbent, N_1^{∞}, increases with the presence of a double bond (1-butene) and decreases for branched compounds (2-methylpropane). It is the same for the isosteric heat of adsorption at infinite dilution given by the Cochran et al. model.

When the pressure approaches the saturation pressure (Figure 4), the difference between the experimental and predicted pressures increases and the standard deviations in the pressure increase.

Conclusion

The automated apparatus allows us to determine adsorption isotherms at pressures up to 4000 kPa. The adsorption equilibria for butane, 2-methylpropane, and 1-butene were measured on activated carbon at relative pressures up to 0.8 P/P_s. For these compounds which have the same number of carbon atoms, the adsorption capacity

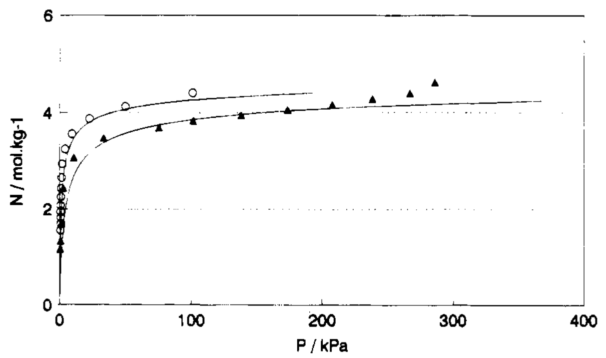

Figure 4. Comparison of 1-butene results at 278 and 303 K with the Flory–Huggins form of the vacancy solution model: ○, 1-butene results at 278 K; ▲, 1-butene results at 303 K; —, Flory–Huggins form of the vacancy solution model.

increases with the presence of a double bond and decreases with a branched structure.

The adsorption equilibria were correlated by the Flory–Huggins form of the vacancy solution model. This model gives good results up to $0.55P/P_s$ and gives temperature-independent parameters but does not describe the range of high pressures.

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