

Adsorption of 2-Methylpropene and 1,3-Butadiene on Activated Carbon

Marie-Georges Olivier,* Karl Berlier, and Jacques Bougard

Service de Thermodynamique, Faculté Polytechnique de Mons, Boulevard Dolez 31, 7000 Mons, Belgium

Four adsorption isotherms at 278, 288, 293, and 303 K of 2-methylpropene and 1,3-butadiene on activated carbon are given. The results at pressures up to $0.8P/P_s$ are measured using 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 the adsorption of 2-methylpropene and 1,3-butadiene on activated carbon. The adsorption of 2-methylpropene and 1,3-butadiene on activated carbon has not been studied previously, but studies have been made on silica gel between 291 and 315 K up to maximum pressures of 80 and 40 kPa, respectively (1).

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 step for studies on binary mixtures of linear or branched, saturated or unsaturated hydrocarbons over a wide range of pressure.

Experimental Section

Supplied by Chemviron Carbon, the adsorbent used in this study is type F30/470 activated carbon whose surface area is $1100 \text{ m}^2\text{g}^{-1}$. 2-Methylpropene and 1,3-butadiene were obtained from Air Liquide Belgium with purities of 99.5 and 99 vol %, respectively.

An automated apparatus, static volumetric type, allowed determination of pure gas isotherms from 273 to 373 K and to pressures of 4000 kPa. In this 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.

The temperature, pressure, and gaseous volume before and after each adsorption step lead 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 (2). The parameters of 2-methylpropene and 1,3-butadiene used in the Redlich-Kwong equation are given in Table 1.

The adsorption apparatus is maintained in a refrigerated incubator regulated to within ± 0.1 K. Pressure measurements are made by an Endress Hauser (Cerabar) absolute transducer. Its pressure range is from 400 to 4000 kPa, and its accuracy is about $\pm 0.1\%$ of the scale. Temperature is measured using a Pt100 with an accuracy of ± 0.1 K. Details of the equipment and the operating procedures are described in the previous publication (3).

Results and Discussion

Equilibrium Results. Adsorption isotherms for 2-methylpropene and 1,3-butadiene on activated carbon at 278, 288, 293, and 303 K are obtained at relative pressures up

Table 1. Critical Temperature (T_c), Critical Pressure (P_c), and Acentric Factor (ω) of 1-Butene, 2-Methylpropene, and 1,3-Butadiene Used in the Redlich-Kwong Equation

	T_c/K	P_c/kPa	ω
1-butene	419.6	4020	0.187
2-methylpropene	417.9	4000	0.190
1,3-butadiene	425.15	4327	0.184

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

$T/\text{K} = 278, P_s/\text{kPa} = 156.99$		$T/\text{K} = 288, P_s/\text{kPa} = 220.73$	
P/kPa	$N/(\text{mol}\cdot\text{kg}^{-1})$	P/kPa	$N/(\text{mol}\cdot\text{kg}^{-1})$
2.79	1.47	1.16	1.43
3.66	1.58	1.18	1.53
4.03	1.70	1.66	1.71
4.53	1.80	1.68	1.89
4.28	1.93	1.90	2.08
4.90	2.04	2.27	2.26
5.14	2.22	2.64	2.44
5.88	2.39	3.39	2.62
6.01	2.62	4.62	2.87
7.74	2.87	6.97	3.11
10.09	3.19	11.42	3.31
16.64	3.51	20.57	3.51
31.72	3.76	32.43	3.66
59.16	3.99	49.36	3.79
107.98	4.24	70.13	3.90
		95.22	4.03
		126.00	4.16
		173.46	4.35

to 0.8. The experimental equilibrium results are presented in Tables 2-5. Several sets of measurements are reproduced with differences of less than 1%. The results for 2-methylpropene and 1,3-butadiene on F30/470 activated carbon at 293 K are shown in Figure 1. The curves are similar in shape and have a classic isotherm form.

The adsorbed gases are composed of molecules containing the same number of carbon atoms but having different degrees of unsaturation and branching. The vapor pressures (P_s) of the 1-butene (3), 2-methylpropene, and 1,3-butadiene 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 second double bond, and when the hydrocarbon has one double bond, the adsorption capacity is not significantly influenced by the branched structure as shown in Figure 1. For the saturated hydrocarbons with four carbons, butane and 2-methylpropane, the amount adsorbed decreased for the branched structure (3).

Correlation. The correlation of the results has two aims. The first one is to obtain physical parameters of a

Table 3. Adsorption Isotherms for 2-Methylpropene on F30/470 Activated Carbon at 293 and 303 K

$T/K = 293, P_0/kPa = 259.16$		$T/K = 303, P_0/kPa = 350.91$	
P/kPa	$N/(mol \cdot kg^{-1})$	P/kPa	$N/(mol \cdot kg^{-1})$
1.48	1.36	1.08	1.09
1.85	1.55	1.82	1.28
2.10	1.74	1.95	1.62
2.22	1.92	2.81	2.18
2.60	2.12	7.88	2.84
2.96	2.32	27.29	3.34
3.58	2.50	60.66	3.61
4.70	2.77	100.46	3.76
7.29	3.02	140.13	3.87
12.61	3.22	175.73	3.97
22.50	3.42	207.87	4.07
34.86	3.58	240.74	4.17
53.52	3.71	266.95	4.31
75.02	3.83	290.31	4.49
99.50	3.93	311.57	4.59
128.05	4.04		
162.04	4.16		
209.63	4.36		

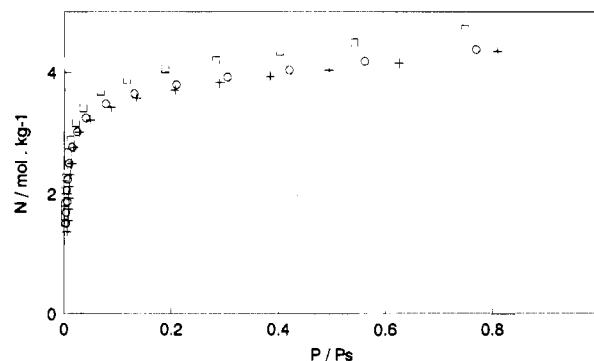
Table 4. Adsorption Isotherms for 1,3-Butadiene on F30/470 Activated Carbon at 278 and 288 K

$T/K = 278, P_0/kPa = 143.47$		$T/K = 288, P_0/kPa = 202.85$	
P/kPa	$N/(mol \cdot kg^{-1})$	P/kPa	$N/(mol \cdot kg^{-1})$
2.10	1.52	0.93	1.04
2.35	1.58	0.95	1.13
2.96	1.70	0.96	1.22
2.98	1.83	1.19	1.39
3.21	1.95	1.21	1.56
3.24	2.08	1.43	1.73
3.33	2.27	1.45	1.90
3.83	2.45	1.46	2.07
4.20	2.63	1.80	2.24
4.57	2.87	2.05	2.49
5.31	3.15	2.92	2.73
8.03	3.51	3.78	3.03
16.56	3.87	6.75	3.38
39.18	4.21	13.55	3.72
77.57	4.56	28.01	4.00
		51.12	4.22
		86.59	4.44
		142.21	4.71

Table 5. Adsorption Isotherms for 1,3-Butadiene on F30/470 Activated Carbon at 293 and 303 K

$T/K = 293, P_0/kPa = 238.76$		$T/K = 303, P_0/kPa = 324.83$	
P/kPa	$N/(mol \cdot kg^{-1})$	P/kPa	$N/(mol \cdot kg^{-1})$
0.37	1.51	0.29	0.90
0.39	1.62	1.16	1.16
0.41	1.74	1.53	1.42
0.50	1.84	1.90	1.67
0.62	2.06	2.15	1.87
0.87	2.27	2.77	2.21
1.49	2.48	3.88	2.50
1.73	2.69	5.73	2.76
2.85	2.90	8.33	3.03
5.07	3.17	14.88	3.32
8.53	3.42	25.14	3.55
16.19	3.68	38.98	3.74
27.81	3.88	58.39	3.88
44.87	4.06	79.85	4.05
67.61	4.21	117.67	4.19
95.92	4.35	156.73	4.31
129.17	4.50	193.93	4.44
178.61	4.72	229.03	4.57
		258.20	4.73
		279.22	4.91

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

**Figure 1.** Adsorption results for 1-butene, 2-methylpropene, and 1,3-butadiene on F30/470 activated carbon at 293 K: \circ , 1-butene (3); $+$, 2-methylpropene; \square , 1,3-butadiene.

same media, without any modification. There are few models satisfying these requirements.

Previous studies (4) 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

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

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

$$\theta = N/N_1^\infty \quad (2)$$

where N and N_1^∞ are the amount adsorbed and the maximum amount adsorbed, respectively. The material within the first set of parentheses of eq 1 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 enthalpy of adsorption at infinite dilution, q_1 , are related theoretically by the following expression:

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

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 amount adsorbed of pure component, N_1^∞ . α_{1v} is the parameter describing

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

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:

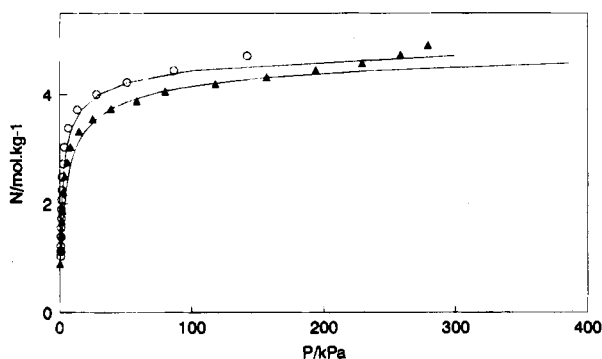
$$\alpha_{1v} = m_1 N_1^\infty - 1 \quad (5)$$

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 a 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 allows

Table 6. Temperature-Independent Regression Parameters for the Flory–Huggins Form of the Vacancy Solution Model on F30/470 Activated Carbon up to $0.5P/P_s$.

adsorbate	$N_{01}^{\infty}/$ (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)	number of experimental results up to $0.50P/P_s$	$\sigma(P)/kPa$
1-butene (4)	5.08	24.9	0.80	3.602	0.84	50	2.86
2-methylpropene	5.15	26.6	1.88	3.29	0.45	58	3.88
1,3-butadiene	5.43	18.7	0.261	3.908	5.21	64	2.37

**Figure 2.** Comparison of 1,3-butadiene results at 288 and 303 K with the Flory–Huggins form of the vacancy solution model: ○, 1,3-butadiene results at 288 K; ▲, 1,3-butadiene results at 303 K; —, Flory–Huggins form of the vacancy solution model.

excellent interpolation within, and reasonable extrapolation outside, 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 isothermal data only (4).

The values of the temperature-independent regression parameters for the VSM-FH are listed in Table 6. The Flory–Huggins form of the vacancy solution model gives good results up to $0.5 P/P_s$.

The parameters have a physical significance. At all temperatures, the maximum amount adsorbed per mass of adsorbent, N_1^{∞} , increases with the presence of a double bond (1-butene to 1,3-butadiene) and is approximately the same for the linear compound (1-butene) and the branched compounds (2-methylpropene). It is the same for the isosteric enthalpy of adsorption at infinite dilution given by the Cochran et al. model. When the pressure approaches the saturation pressure, the difference between

the experimental and predicted pressures increases and also the standard deviations ($\sigma(P)$) in the pressure increase (Figure 2).

Conclusion

The adsorption equilibria for 2-methylpropene and 1,3-butadiene were measured on activated carbon at relative pressures up to $0.8 P/P_s$. For these compounds and previously measured 1-butene having the same number of carbon atoms, the adsorption capacity increases with the presence of a second double bond, and when the compounds have one double bond, the adsorption capacity is not significantly influenced by 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 $0.5 P/P_s$, and gives temperature-independent parameters but does not describe the range of high pressures.

Literature Cited

- (1) Cortés, J.; Alzamora, L.; Troncoso, G.; Prieto, A. L.; Valencia, E. *J. Chem. Soc., Trans. Faraday 1* 1984, 80, 2127.
- (2) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986; Vol. 234, pp 158–161.
- (3) Olivier, M.-G.; Berlier, K.; Jadot, R. Adsorption of butane, 2-methyl propane and 1-butene on activated carbon. *J. Chem. Eng. Data*, in press.
- (4) Cochran, T. W.; Kabel, R. L.; Danner, R. P. *AIChE J.* 1985, 31 (2), 268–277.
- (5) *NAG Mini Manual Mark 15*; Numerical Algorithms Group: Oxford, 1991.

Received for review April 20, 1994. Accepted July 29, 1994.* This paper presents results of the Belgian Programme on Interuniversity Poles of Attraction initiated by Belgian State, Prime Minister's, Science Policy Programming. The scientific responsibility is assumed by its authors.

* Abstract published in *Advance ACS Abstracts*, September 1, 1994.