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Adsorption of Light Hydrocarbons and Carbon Dioxide on Silica Gel

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Adsorption isotherms of methane, ethane, ethylene, propane, propadiene, butane, 2-methylpropane, and carbon dioxide on silica gel are given at three temperatures (278 K, 293 K, and 303 K). The results at pressures up to $0.8P/P_s$ for the subcritical compounds and up to 3500 kPa for the supercritical compounds are measured using an automated apparatus.

Introduction

The main component of natural gas is methane, but small quantities of other gases, such as ethane, ethylene, propane, propadiene, butane, 2-methylpropane, and carbon dioxide, are also present. These compounds are in negligible quantities in natural gas but can become a problem for the storage of methane by adsorption, being less volatile than methane and so preferentially occupying the active sites of adsorbents. Information concerning component removal by adsorption is provided by natural adsorptive storage which, in this case, is an adsorption (high pressure)/desorption (low pressure) cycle of a complex mixture formed essentially of light and heavy hydrocarbon compounds. To solve the problem of these pollutants, it is necessary to know the equilibria of these compounds on the same adsorbent near the ambient temperature and over a wide range of pressures.

An automated volumetric apparatus was built by Berlier et al. (1995), allowing the measurement of obtained pure-component isotherms over a wide range of pressures from (0 to 4000) kPa and between (273 and 373) K.

The present study is devoted to the measurement of adsorption of methane, ethane, ethylene, propane, propadiene, butane, 2-methylpropane, and carbon dioxide on silica gel.

In the literature, one may find measurements for methane, ethane, and ethylene on Davison type silica gel by Lewis et al. (1950), Gilmer and Kobayashi (1964, 1965), Haydel and Kobayashi (1967), Mason and Cooke (1966), and Masukawa and Kobayashi (1968) at pressure up to 4000 kPa or 0.8 of the relative pressure and at one or several temperatures. Data for propane, butane, and 2-methylpropane are scarce and limited to low pressures (Mason and Cooke, 1966; Lewis et al., 1950; Al-Sahhaf et al., 1981). Carbon dioxide has been studied on Unilever type silica gel at one low temperature (195 K) up to $0.5P_{sat}$ (Lemcoff and Sing, 1977). Propadiene has never been studied on this adsorbent. In summary, a systematic study of the adsorption equilibrium of these compounds on the same silica gel and at the same conditions of pressure and temperature has never been done.

Experimental Section

Supplied by Kali-Chemie AG, the adsorbent used in this study is a KC type silica gel. Internal measurements have been conducted in our department on a Quantasorb sorption analyzer to characterize the geometric structure using a conventional technique. The BET specific surface was 750 $m^2 \cdot g^{-1}$. The light hydrocarbons were obtained from Air Liquide Belgium with purities of 99.5 volume %.

Table 1. Critical Temperature (T_c), Critical Pressure (P_c), Critical Molar Volume (v_c), and Acentric Factor (ω) of Studied Compounds (Prausnitz et al., 1986)

adsorbant	T_c/K	P_c/kPa	v_c/cm^3 mol^{-1}	ω
methane	190.6	4600	99	0.008
ethane	305.4	4880	148	0.098
ethylene	282.4	5040	129	0.085
propane	369.8	4240	203	0.152
propadiene	393.0	5470	162	0.313
butane	425.2	3800	255	0.193
2-methylpropane	408.1	3650	263	0.176
carbon dioxide	304.2	7380	94	0.225

An automated apparatus of a static volumetric type allowed the determination of pure gas isotherms from 273 K 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 were determined by appropriate $P-T-V$ measurements.

The temperature, pressure, and gaseous volume before and after each adsorption step provide the moles of the gas before and after adsorption and finally, by subtraction, the quantity adsorbed. The calculation of the gaseous moles was performed using the Redlich−Kwong equation of state (Prausnitz et al., 1986). The parameters of the light hydrocarbons used in the Redlich−Kwong equation are given in Table 1.

The adsorption apparatus was maintained in a refrigerated incubator regulated to within 0.1 K. Pressure measurements were made by an Endress Hauser (Cerabar) absolute transducer. Its pressure range is from (400 to 4000) kPa and its accuracy is about 0.1% of the scale. The temperature was measured using a 100 Ω Pt resistance thermometer with an accuracy of 0.1K.

The error in the moles adsorbed is due to the accuracy of the equation of state used for the calculation of the vapor molar volumes (<1%), the experimental error of the mass of adsorbent due to the accuracy of the balance ($\pm 5 \times 10^{-4}$ %), the experimental error in the temperature (±0.05%), the experimental error on the gas volume (estimated to be less than ±1%), and the experimental error in the pressure (variable). The prime source of error is in the pressure measurement, and this results in a maximum relative error in the moles adsorbed of ±5% with a typical value of 3%. Such experimental errors are common for the volumetric method in which the moles adsorbed are not directly measured (Frère et al., 1994).

Details of the equipment and the operating procedures are described in a previous publication (Berlier et al., 1995).

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Table 2. Experimental Adsorption Isotherms of Methane on Silica Gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
87.75	0.13	71.88	0.10	70.25	0.06
185.63	0.26	152.88	0.19	174.88	0.14
288.00	0.39	228.25	0.26	277.25	0.22
390.38	0.50	322.75	0.36	371.75	0.29
492.75	0.60	415.00	0.43	455.00	0.35
586.13	0.70	525.25	0.51	552.88	0.41
667.13	0.77	641.13	0.60	663.13	0.49
745.88	0.84	751.38	0.68	764.38	0.55
883.13	0.96	850.38	0.77	856.63	0.61
1012.25	1.06	944.88	0.83	966.88	0.68
1130.63	1.15	1031.50	0.87	1067.00	0.74
1236.38	1.22	1149.63	0.96	1158.13	0.79
1327.50	1.29	1273.38	1.03	1244.75	0.84
1416.38	1.35	1389.25	1.09	1347.13	0.90
1503.00	1.40	1497.25	1.15	1443.87	0.95
1624.50	1.48	1599.63	1.24	1544.00	1.00
1744.88	1.55	1702.00	1.29	1646.38	1.05
1861.88	1.62	1802.13	1.33	1743.13	1.10
1974.38	1.69	1896.63	1.38	1839.88	1.15
2084.63	1.75	2068.75	1.45	2014.25	1.24
2187.00	1.81	2225.13	1.55	2177.38	1.31
2287.13	1.86	2370.25	1.63	2324.75	1.38
2459.25	1.95	2505.25	1.68	2459.75	1.44
2611.13	2.02	2626.75	1.75	2581.25	1.50
2742.75	2.09	2737.00	1.82	2694.88	1.54
2858.63	2.14	2842.75	1.85	2799.50	1.59
2964.38	2.19	2976.63	1.91	2936.75	1.65
3091.50	2.26	3095.88	1.96	3058.25	1.70
3223.13	2.34	3230.88	2.03	3222.50	1.76
3408.78	2.43	3414.25	2.12	3419.38	1.84

Table 3. Experimental Adsorption Isotherms of Ethane on Silica Gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
41.13	0.40	70.56	0.41	87.62	0.37
221.59	1.30	243.75	0.99	275.69	0.86
436.44	1.98	421.19	1.46	471.19	1.25
648.94	2.54	598.63	1.85	665.63	1.61
859.88	2.98	773.94	2.16	856.88	1.91
1065.34	3.35	940.75	2.47	1041.75	2.14
1263.00	3.67	1098.00	2.71	1217.06	2.34
1449.72	3.92	1258.44	2.97	1379.63	2.55
1627.06	4.10	1410.38	3.17	1533.69	2.72
1793.47	4.26	1552.75	3.33	1679.25	2.81
1946.59	4.36	1685.56	3.47	1813.13	2.93
2088.00	4.37	1806.69	3.64	1940.63	3.00
2211.44	4.34	1971.38	3.81	2054.31	3.14
2321.59	4.27	2115.88	3.97	2214.75	3.28
2416.91	4.17	2243.38	4.14	2353.94	3.41
2493.47	4.14	2397.44	4.28	2478.25	3.56
		2557.88	4.42	2623.81	3.79
		2735.31	4.62	2783.19	3.99
		2936.13	4.87	2958.50	4.22
		3186.88	5.23	3194.38	4.55

Results and Discussion

Equilibrium Results. Adsorption isotherms on silica gel at 278 K, 293 K, and 303 K were obtained at relative pressures up to 0.8 for subcritical compounds (ethane, propane, propadiene, butane, and 2-methylpropane) and at absolute pressures up to 3500 kPa for supercritical compounds (methane and ethylene). The experimental equilibrium results are presented in Tables 2−9. Several sets of measurements were reproduced with differences less than 1%.

The adsorption of propylene, 2-methylpropene, 1-butene, and 1,3-butadiene was measured, but satisfactory data for these compounds were not obtained on this silica gel. Polymerization effects or chemical interaction of the double bond in these components with polar hydroxyl groups on the surface of this adsorbent is apparently encountered; only a fraction of the material originally adsorbed could be recovered, and the activity of the silica gel was greatly reduced thereafter.

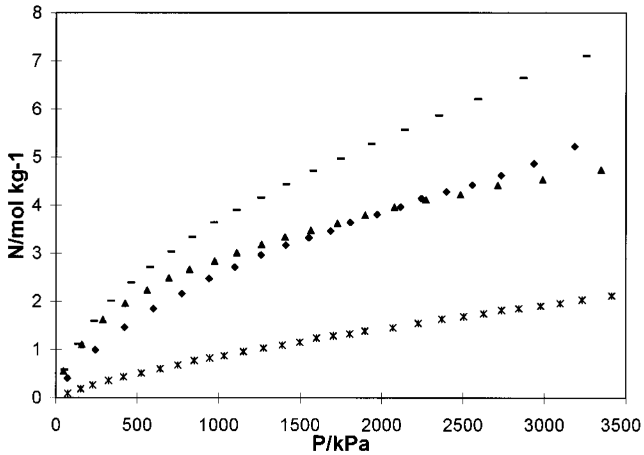

Figure 1. Experimental adsorption isotherms of methane (*), ethane (♦), ethylene (▲), and carbon dioxide (−) on KC type silica gel at 293 K.

Table 4. Experimental Adsorption Isotherms of Ethylene on Silica Gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
25.88	0.62	45.09	0.56	70.62	0.58
82.13	1.17	157.75	1.18	230.31	1.17
153.00	1.59	287.91	1.62	404.22	1.60
230.63	1.94	424.63	1.96	582.50	1.94
317.25	2.21	560.25	2.23	761.88	2.19
446.63	2.56	692.59	2.48	934.69	2.43
556.88	2.81	821.66	2.67	1102.03	2.62
670.50	3.03	973.69	2.84	1256.25	2.82
864.00	3.33	1109.31	3.01	1405.00	2.99
1055.25	3.61	1260.25	3.19	1546.09	3.13
1263.38	3.84	1405.72	3.34	1676.25	3.28
1373.63	3.98	1563.22	3.48	1856.72	3.48
1476.00	4.08	1726.19	3.63	2024.06	3.65
1674.00	4.24	1896.81	3.80	2178.28	3.78
1864.13	4.42	2077.28	3.96	2317.19	3.88
2047.50	4.56	2270.88	4.11	2486.72	4.00
2214.00	4.71	2483.06	4.22	2667.19	4.13
2365.88	4.85	2714.94	4.41	2853.13	4.28
2505.38	4.96	2989.47	4.54	3075.16	4.44
2632.50	5.03	3348.22	4.74	3354.06	4.69
2742.75	5.13				
2883.38	5.25				
3028.50	5.36				
3179.25	5.49				
3395.25	5.68				

The results for methane, ethane, ethylene, and carbon dioxide at 293 K are shown in Figure 1.

Figure 2 gives the experimental results for propane, propadiene, butane, and 2-methylpropane at 303 K on the same adsorbent. The curves are similar in shape and have a classic isotherm form.

The adsorption capacity of the silica gel for carbon dioxide is greater than for ethane, ethylene, and methane. This phenomenom is due to the interaction between the two double bonds of carbon dioxide and the polar sites of the silica gel.

In the range of pressures below 2000 kPa and at 293 K, silica gel has a greater adsorption capacity for ethylene

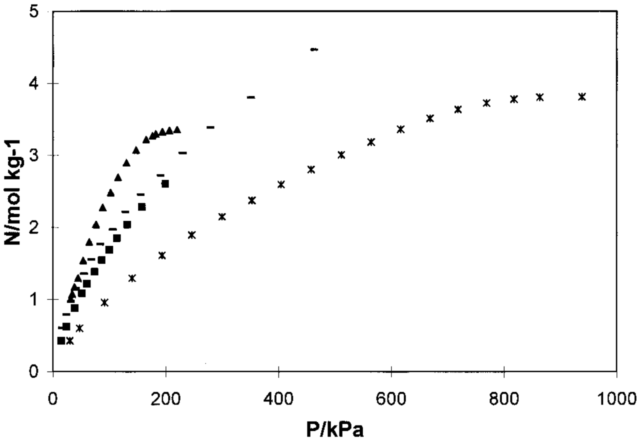

Figure 2. Experimental adsorption isotherms of propane (*), propadiene (—), *n*-butane (▲), and isobutane (■) on KC type silica gel at 303 K.

Table 5. Experimental Adsorption Isotherms of Propane on Silica gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
16.38	0.52	19.50	0.45	29.84	0.43
23.13	0.66	32.72	0.65	47.38	0.60
34.75	0.87	48.47	0.84	91.03	0.96
46.00	1.08	72.66	1.11	139.50	1.30
58.56	1.27	99.09	1.36	192.78	1.61
70.75	1.47	126.38	1.60	246.41	1.89
84.63	1.65	154.78	1.82	299.34	2.14
103.38	1.88	182.63	2.03	351.94	2.37
122.69	2.08	218.91	2.28	403.84	2.60
145.19	2.33	254.63	2.51	457.47	2.80
170.31	2.60	297.09	2.76	510.75	3.01
200.31	2.92	345.47	3.00	564.38	3.19
239.88	3.26	400.59	3.30	616.28	3.37
293.88	3.72	470.91	3.63	668.19	3.52
421.38	4.12	566.53	3.94	718.38	3.64
				768.56	3.73
				817.03	3.78
				863.44	3.81
				938.38	3.81
				1003.34	3.74

Table 6. Experimental Adsorption Isotherms of Propadiene on Silica gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
8.92	0.87	8.74	0.67	15.65	0.61
13.68	1.09	13.24	0.86	23.53	0.79
18.18	1.30	19.43	1.07	31.84	0.97
23.93	1.47	26.74	1.28	41.46	1.15
29.30	1.61	36.68	1.50	55.03	1.35
36.55	1.78	49.24	1.76	67.71	1.55
43.93	1.94	63.49	2.00	83.90	1.76
52.30	2.12	81.49	2.28	105.78	1.97
63.80	2.35	100.80	2.54	127.65	2.21
74.68	2.58	125.93	2.82	156.09	2.45
91.05	2.85	157.80	3.15	191.31	2.72
108.3	3.16	196.43	3.52	229.59	3.03
132.68	3.53	243.68	3.95	279.24	3.39
168.55	4.04	311.93	4.48	349.68	3.80
238.93	4.89	431.74	5.26	463.21	4.47

Table 7. Experimental Adsorption Isotherms of Butane on Silica Gel KC at 278 K, 288 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}	*P*/kPa	*N*/ mol·kg^{-1}
5.48	0.69	13.98	0.90	31.00	1.00
12.35	1.21	26.73	1.47	33.91	1.07
19.41	1.63	42.48	1.97	38.22	1.17
26.16	1.96	58.23	2.39	43.56	1.29
32.98	2.23	74.92	2.77	53.03	1.54
39.60	2.48	91.51	3.08	64.47	1.79
46.35	2.71	108.48	3.31	76.38	2.04
51.10	2.93	129.11	3.43	88.47	2.27
57.54	3.14	148.70	3.47	101.97	2.49
63.85	3.30	163.51	3.48	115.00	2.70
72.23	3.42	173.83	3.48	130.47	2.90
82.23	3.50	180.11	3.49	147.34	3.07
91.23	3.53	184.23	3.49	165.06	3.22
98.85	3.54	192.76	3.50	175.84	3.27
109.66	3.57			182.41	3.30
				193.84	3.33
				205.75	3.35
				219.91	3.36

Table 8. Experimental Adsorption Isotherms of 2-Methylpropane on Silica Gel KC at 278 K, 293 K, and 303 K

T/K = 278		*T*/K = 293		*T*/K = 303	
P/kPa	*N*/mol·kg^{-1}	*P*/kPa	*N*/mol·kg^{-1}	*P*/kPa	*N*/mol·kg^{-1}
7.81	0.58	13.19	0.54	14.78	0.43
8.75	0.65	16.47	0.63	24.44	0.62
9.75	0.71	19.94	0.73	38.31	0.88
12.00	0.80	23.59	0.82	51.16	1.08
14.13	0.89	29.22	0.96	60.44	1.22
16.31	0.98	35.41	1.09	73.00	1.38
19.06	1.09	41.50	1.22	86.22	1.55
22.94	1.23	50.41	1.39	98.50	1.69
26.13	1.40	59.03	1.55	112.66	1.85
30.44	1.59	70.28	1.75	131.03	2.04
38.75	1.84	83.97	1.97	157.00	2.29
50.38	2.20	105.06	2.24	198.72	2.61
83.00	2.78	132.81	2.61		
		216.06	2.92		

Table 9. Experimental Adsorption Isotherms of Carbon Dioxide on Silica Gel KC at 293 K and 303 K

T/K = 293		*T*/K = 303	
P/kPa	*N*/mol·kg^{-1}	*P*/kPa	*N*/mol·kg^{-1}
52.56	0.58	47.50	0.52
136.78	1.11	293.59	1.53
235.22	1.59	548.44	2.21
340.22	2.01	802.19	2.74
462.72	2.38	1097.50	3.24
580.84	2.71	1358.91	3.69
708.81	3.03	1643.28	4.11
838.97	3.33	1927.66	4.52
971.31	3.64	2226.25	4.97
1110.22	3.90	2539.06	5.40
1258.97	4.16	2850.78	5.77
1413.19	4.44	3176.72	6.18
1579.44	4.71		
1747.88	4.97		
1936.00	5.28		
2141.63	5.57		
2350.53	5.87		
2592.25	6.21		
2871.16	6.65		
3258.34	7.11		

than for ethane. Although, at this temperature, ethane is subcritical and ethylene supercritical, ethylene is the more strongly adsorbed gas. The silica gel shows a strong preference for the more unsaturated compound. Similar effects are shown in Figure 2 for propane and propadiene. These compounds contain the same number of carbon atoms but have different degrees of saturation. The vapor pressures of the two components are approximately equal, and the effect of the differences in structure is dominant.

In the range of high pressures, above 2000 kPa at 293 K, this effect is reversed for ethane and ethylene. At these pressures, which correspond to multilayer adsorption, the properties of the pure gases are the major factor compared to the interaction between the adsorbent and the gas.

Figure 2 also gives data for butane and 2-methylpropane. In this case, 2-methylpropane has a higher vapor pressure at a given temperature than does butane, and thus, the effect of the vapor pressure and the preference for a linear structure results in KC silica gel having a greater adsorption capacity for butane than for 2-methylpropane.

Conclusion

Three isotherms for light hydrocarbons and two for carbon dioxide have been determined in a wide range of pressures on KC type silica gel using an automated apparatus. On this adsorbent, the adsorption capacity depends essentially on the interaction between the surface of the adsorbent and the gas. The unsaturated compounds are preferentially adsorbed, and several of these react chemically with the adsorbent such as propylene, 1-butene, 2-methylpropene, and 1,3-butadiene.

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