Adsorption of 1,2-Dichloropropane on Activated Carbon

J. Zhang,† W. Zhu, M. Makkee,* B. van der Linden, F. Kapteijn, and J. A. Moulijn

Industrial Catalysis, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

The adsorption of 1,2-dichloropropane vapor on activated carbon has been investigated using a novel technique, TEOM. The adsorption isotherms are for the first time reported at temperatures in the range from 303 to 473 K and at pressures up to 6 kPa. The Toth isotherm appropriately describes the equilibrium data. The thermodynamic properties such as the Henry law constant and enthalpy associated with adsorption are derived to characterize interactions between adsorptive and adsorbent.

Introduction

The disposal of liquid wastes containing chlorinated compounds, which are recognized as extremely toxic to aquatic life and resistant to biodegradation, is a problem of great urgency.[1] To prevent pollution by these materials, usually they are incinerated. Incineration is effective, but it is expensive and does not recover any value from the waste materials.

1,2-Dichloropropane is one of these widespread chlorinated pollutants. A process based on the hydrodechlorination of 1,2-dichloropropane to propene has received considerable attention in recent years.[2] Some metals such as platinum and palladium supported on activated carbon have been used as catalysts for this process,[3] which makes it possible to economically recycle the 1,2-dichloropropane back to useful products, such as propylene, at high yield.

This work addresses the fundamental science of this important process. Adsorption equilibrium is, on one hand, the key information for the design of practical separation processes based on adsorption mechanisms. The adsorption isotherm data are, on the other hand, of utmost importance for modeling the catalytic hydrodechlorination process, for instance, studies in catalytic kinetics and catalyst deactivation. However, up to now there has been hardly any data available concerning the adsorption properties of 1,2-dichloropropane on activated carbon.

This paper presents experimental results for the adsorption of 1,2-dichloropropane on activated carbon determined by the inertial microbalance technique, TEOM.[4] Furthermore, thermodynamic properties, like the enthalpy and Henry's law constant associated with adsorption, are presented to characterize interactions between adsorptive and adsorbent.

Experimental Section

Adsorption. A Rupprecht & Patashnick TEOM 1500 mass analyzer was used in an experimental setup designed for measurement of equilibrium and transient adsorption on microporous materials. A detailed description of the TEOM apparatus is given elsewhere,[4] and the TEOM technique for accurately measuring adsorption properties has been verified by Zhu et al.[5]

Table 1. Textural Properties of the Investigated Activated Carbon

property	value
total pore volume, $cm^3\ g^{-1}$	0.664
micropore volume, $cm^3\ g^{-1}$	0.493
special surface area, $m^2\ g^{-1}$	1180 ± 40
mean pore size, nm	1.21

A sample of 16.4 mg of the adsorbent particles was used for the adsorption experiments. Quartz wool was used at the top and bottom of the sample bed to keep the adsorbent particles firmly packed, which is essential for a stable measurement. The isotherms were obtained by a stepwise increase of the partial pressure of the feed vapor at fixed temperatures. The partial pressure of the feed vapor was determined by its fraction of the total molar-feed-flow rate through the sample bed and the total pressure. A mixture of nitrogen and the sample vapor was used to establish the partial pressure.

The isotherm data were accurately measured for partial pressures up to 6 kPa, which is much lower than the saturation vapor pressure of 1,2-dichloropropane at room temperature. It is necessary to prevent the condensation of the adsorptive vapor during its transfer in piping lines. The temperature range covered was from 303 to 473 K. Five temperatures were used to reduce the uncertainty in the derived thermodynamic properties. Most experiments were duplicated, and both adsorption and desorption experiments were performed to confirm reversibility.

The temperature in the sample bed was controlled with an accuracy of ±0.5 K, and the deviation of a component concentration in the inlet of the sample bed was within 0.2%. The TEOM microbalance measurements were accurate to 1 μg.

Prior to the experiments the adsorbent particles were outgassed in the following way. After a temperature rise with a rate of 10 K min^{-1} in situ in a nitrogen flow rate of 200 $cm^3\ min^{-1}$, the sample was heated at 502 K for 24 h in order to remove adsorbed impurities.

Nitrogen was obtained as an ultrahigh purity gas (>99.999%). The liquid 1,2-dichloropropane had a purity of 99% (Fluka).

Adsorbent. The activated carbon from Calgon Carbon Corporation and designated BPLF-3 was used as the

* To whom correspondence should be addressed. Fax: +31-15-2784452. E-mail: M.Makkee@tnw.tudelft.nl.
† Present address: Zhejiang Chemical Industrial Research Institute, 310023 Hangzhou, Zhejiang, P. R. of China.

10.1021/je0003400 CCC: $20.00
Published on Web 04/06/2001

Table 2. Experimental Isotherm Data for 1,2-Dichloropropane on Activated Carbon

p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}
T = 303 K		T = 338 K		T = 373 K		T = 423 K		T = 473 K	
0.3427	1.9267	0.3559	1.2594	0.3651	0.5874	0.3849	0.3102	0.3981	0.1175
0.5134	2.1711	0.5332	1.4662	0.5470	0.7237	0.5766	0.3853	0.5964	0.1551
0.6837	2.3449	0.7100	1.6353	0.7284	0.8365	0.7678	0.4525	0.7941	0.1833
0.8535	2.4530	0.8863	1.7556	0.9093	0.9305	0.9586	0.4944	0.9914	0.2054
1.0229	2.5799	1.0622	1.8581	1.0898	0.9803	1.1488	0.5503	1.1881	0.2162
1.1918	2.6612	1.2377	1.9577	1.2697	1.0818	1.3385	0.5954	1.3843	0.2547
1.5284	2.7937	1.4126	2.0324	1.4493	1.1316	1.5277	0.6297	1.5801	0.2693
1.7821	2.8510	1.5872	2.1109	1.6283	1.2030	1.7165	0.6767	1.7753	0.2923
2.1239	2.9159	1.8313	2.2044	1.8663	1.2768	1.9576	0.7265	2.0347	0.3163
2.5752	2.9991	2.1936	2.3167	2.2458	1.3440	2.3329	0.7810	2.4199	0.3407
3.2134	3.1062	2.7723	2.4243	2.8411	1.4685	2.9556	0.8623	3.0243	0.3839
3.5572	3.1438	3.2543	2.4803	3.2951	1.5268	3.4313	0.9253	3.5130	0.4145
3.6790	3.1551	3.6185	2.5766	3.6798	1.6034	3.8025	0.9662	3.8945	0.4370
4.3900	3.2730	3.7590	2.6024	3.8230	1.6198	3.9350	0.9826	4.0469	0.4474
4.8735	3.3012	4.5065	2.7204	4.6036	1.7199	4.7008	1.0526	4.7785	0.4737
5.1615	3.3228	5.0040	2.7979	5.0910	1.7857	5.2216	1.0982	5.2651	0.5066
		5.2772	2.8130	5.3930	1.8120	5.5087	1.1194	5.5550	0.5202

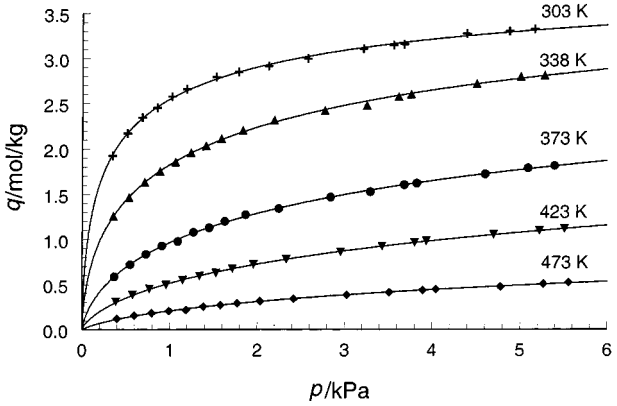

Figure 1. Adsorption isotherms of 1,2-dichloropropane on activated carbon. Lines are the Toth isotherm model fits.

adsorbent. The textural properties of the activated carbon investigated are listed in Table 1.

Results and Discussion

Isotherms. The isotherm data of 1,2-dichloropropane adsorbed on the activated carbon are presented in Table 2. The isotherms were reversible over the complete pressure range investigated. For the sake of clarity, the desorption data are omitted.

For practical utility, the experimental data should be correlated by an analytical expression that includes adjustable parameters as a function of temperature. Various empirical methods have been proposed to fit isotherm data. In many cases, however, it may not be easy to determine a set of isotherm parameters that can represent all the experimental data at multiple temperatures with good accuracy.

The isotherms of 1,2-dichloropropane on the activated carbon exhibit a type-I adsorption isotherm (Brunauer classification) over the temperature and pressure range studied, as shown in Figure 1. For adsorption on heterogeneous adsorbents such as activated carbon, the Toth model is often used to fit isotherm data.[6−7]

$$q = q_{sat}\frac{kp}{[1 + (kp)^t]^{1/t}} \qquad (1)$$

where q is the amount adsorbed, q_{sat} is the saturation amount adsorbed, k is the equilibrium constant, p is the pressure, and t is the parameter that characterizes the system heterogeneity. Being the three-parameter model, the Toth equation can describe well the isotherm data, also included in Figure 1. The estimated values of the adsorption parameters in the Toth model are listed in Table 3. The fitted values of equilibrium parameters show the temperature dependence. For the equilibrium constant, k, the value decreases with an increase in the operating temperature. However, the fitted values of q_{sat} and t do not regularly show changes with changes in temperature. This behavior emphasizes a difficulty in applying the Toth model in a strict way. Similar results fitted with the Toth equation for adsorption on activated carbon have been reported.[6,7] Because of its simplicity in form and its correct behavior at low and high pressures, the Toth model is usually recommended as the first choice of isotherm equations for fitting adsorption data.[6]

Table 3. Fitted Values and Standard Deviations of Adsorption Equilibrium Constants (Eq 1) and the Estimated Values of the Henry Law Constant (Eq 2)

T / K	q_{sat} / mol kg^{-1}	k / kPa^{-1}	t	σ_{model}[a] / mol kg^{-1}	K_H / mol kg^{-1} kPa^{-1}
303	4.31 ± 0.15	17.7 ± 4.7	0.46 ± 0.04	0.02	146
338	5.20 ± 0.45	7.99 ± 2.08	0.37 ± 0.04	0.02	17.0
373	4.56 ± 0.58	1.72 ± 0.22	0.38 ± 0.04	0.01	3.31
423	5.65 ± 1.15	0.76 ± 0.05	0.31 ± 0.03	0.01	1.21
473	3.24 ± 1.69	0.29 ± 0.04	0.34 ± 0.08	0.01	0.37

[a] Standard deviation model: $\sqrt{\sum_n (q_{cal} - q_{exp})^2/(n-j)}$, for j fitting parameters.

Other isotherm models, such as the Unilan model[7] and those based on the theory of micropore volume filling introduced and developed by Dubinin,[8] have also been considered, but from the fitting results the Toth model describes the present case best over the full range. For engineering purposes the Toth isotherm is quite attractive to be applied due to its simplicity.

Thermodynamic Properties. From the isotherm data a number of thermodynamic properties have been derived. The Henry's law constant, K_H, quantifies the extent of adsorption of a given adsorptive by a solid. The magnitude of K_H depends on the properties of both the adsorptive and the solid. An alternative way of representing the equilibrium data to extract the Henry's law constant makes use of the virial form of the thermodynamic equilibrium relation.[9]

$$p = \frac{q}{K_H}\exp\left(2A_1q + \frac{3}{2}A_2q^2 + \frac{4}{3}A_3q^3 + ...\right) \qquad (2)$$

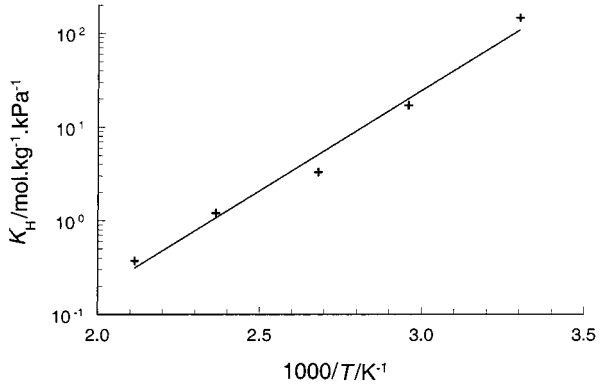

Figure 2. ln K_H versus 1/T plot for the studied adsorptive by activated carbon.

where K_H is the Henry's law constant, q is the amount adsorbed, p is the equilibrium pressure, and A_i is the virial coefficient. It is evident that $\ln(p/q)$ versus q should approach linearity at low loadings, thus providing a straightforward extrapolation to determine the Henry's law constant K_H. The K_H values obtained in this way at the different temperatures, included in Table 3, can be described with the integrated form of the van't Hoff equation

$$K_H = K_{H0} \exp\left(\frac{-\Delta H^\circ}{RT}\right) \quad (3)$$

The observed linearity of the ln K_H versus 1/T plot (Figure 2) leads to the enthalpy of adsorption at zero coverage, ΔH°, and the pre-exponential factor, K_{H0}. The estimated values of ΔH° and K_{H0} are -41.0 kJ mol^{-1} and 9.3×10^{-6} mol kg^{-1} kPa^{-1}, respectively.

Conclusion

The equilibrium adsorption data of 1,2-dichloropropane on activated carbon have been accurately measured by means of the TEOM technique. The isotherms are for the first time reported in the temperature range from 303 to 473 K and at pressures up to 6 kPa. The Toth isotherm expression appropriately describes the equilibrium data. The reported experimental data might be useful for either the design of the adsorption-based process for the disposal of wastes containing 1,2-dichloropropane or modeling the catalytic hydrodechlorination process.

Acknowledgment

The authors are indebted to The DOW Chemical Company for funding this project.

Literature Cited

(1) Bershveren, K. *Handbook of Environmental Data on Organic Chemicals*; Van Nostrand Reihold: New York, 1989.
(2) Smith, D. D.; Holbrook, T. T.; Harley, A. D.; Ito, N. L. Hydrodehalogenation Process and Catalyst for Use Herein. U.S. Patent 5,430,214, 1995.
(3) Harley, A. D.; Holbrook, T. M.; Smith, D. D.; Cinneros, D. D.; Ito, N. L.; Mouchison, C. B. Process for Converting Chlorinated Byproducts and Waste Products to Useful Materials. U.S. Patent 5,453,557, 1995.
(4) Zhu, W.; Van de Graaf, J. M.; Van den Broeke, L. J. P.; Kapteijn, F.; Moulijn, J. A. TEOM: A Unique Technique for Measuring Adsorption Properties. Light Alkanes in Silicalite-1. *Ind. Eng. Chem. Res.* **1998**, *37*, 1934.
(5) Zhu, W.; Kapteijn, F.; Moulijn, J. A. Equilibrium Adsorption of Light Alkanes in Silicalite-1 by the Inertial Microbalance Technique. *Adsorption* **2000**, *6*, 159.
(6) Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press: London, 1998.
(7) Valenzuela, D. P.; Myers, A. L. *Adsorption Equilibrium Data Handbook*; Prentice Hall: Upper Saddle River, NJ, 1989.
(8) Dubinin, M. M. The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces. *Chem. Rev.* **1960**, *60*, 235.
(9) Ross, S.; Olivier, J. P. *On Physical Adsorption*; John Wiley & Sons: New York, 1964.

Received for review October 16, 2000. Accepted January 31, 2001.

JE0003400