Adsorption isotherms (Item No.: P3040801)

Curricular Relevance
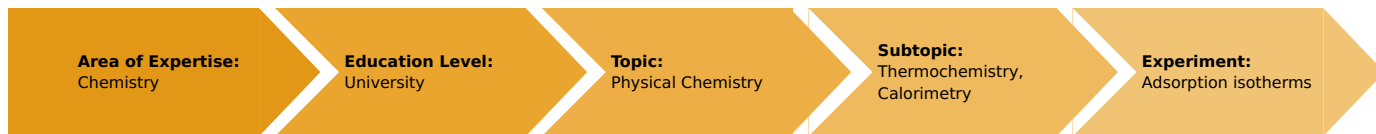
| Area of Expertise: Chemistry | Education Level: University | Topic: Physical Chemistry | Subtopic: Thermochemistry, Calorimetry | Experiment: Adsorption isotherms |

Difficulty	**Preparation Time**	**Execution Time**	**Recommended Group Size**
Difficult	10 Minutes	20 Minutes	2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

adsorbent and adsorbate, Henry, Freundlich and Langmuir adsorption isotherms, volumetry

Overview

Short description

Principle

In general, the term adsorption is used to describe the attachment of gases or dissolved substances to the surface of a solid or liquid. At constant temperature, the quantity of adsorbed substances is a function of the type of system investigated and the partial pressure and / or concentration of the substance concerned. This correlation is described by a number of adsorption isotherms. Their validity is to be investigated experimentally.

Fig. 1: Experimental set-up

Safety instructions
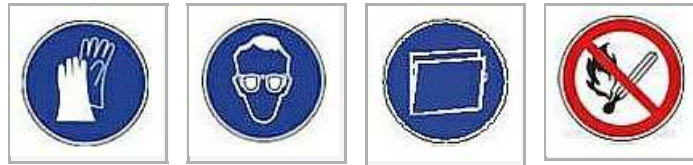
Citric acid
H319: Causes serious eye irritation
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.

Phenolphthalein, 0.5% solution
H226: Flammable liquid and vapour
H319: Causes serious eye irritation
P280: Wear protective gloves/protective clothing/eye protection/face protection
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.
P308+313: If exposed: Call a POISON CENTER or doctor/physician.

Caustic soda solution, 1 M
H290: May be corrosive to metals
H314: Causes severe skin burns and eye damage
P280: Wear protective gloves/protective clothing/eye protection/face protection

PHYWE excellence in science

Robert-Bosch-Breite 10
D - 37079 Göttingen

Tel: +49 551 604 - 0
Fax: +49 551 604 - 107

info@phywe.de
www.phywe.com

Equipment

Position No.	Material	Order No.	Quantity
1	Retort stand, h = 750 mm	37694-00	2
2	Burette clamp, roller mount., 2 pl.	37720-00	1
3	Holder for 2 funnels, PP	33401-00	1
4	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	2
5	Magnetic stirring bar 30 mm, cylindrical	46299-02	2
6	Separator for magnetic bars	35680-03	1
7	Burette, lateral stopcock, Schellbach, 50 ml, graduations 0, 1 ml	36513-01	1
8	Volumetric flask 1000ml, IGJ24/29	36552-00	1
9	Volumetric flask 250 ml, IGJ14/23	36550-00	6
10	Volumetric pipette, 10 ml	36578-00	1
11	Volumetric pipette, 25 ml	36580-00	1
12	Volumetric pipette, 50 ml	36581-00	1
13	Volumetric pipette, 100 ml	36582-00	1
14	Graduated pipette 25 ml	36602-00	1
15	Pipettor	36592-00	1
16	Pipette dish	36589-00	1
17	Erlenmeyer IGJ29/32,boro.,250ml	46126-00	6
18	Stopper, PP, for IGJ 29/32	47508-00	6
19	Erlenmeyer wide neck,boro.,250ml	46152-00	7
20	Beaker, high, BORO 3.3, 100 ml	46026-00	7
21	Funnel, glass, top dia. 55 mm	34457-00	7
22	Circular filter,d 90 mm,100 pcs	32977-03	1
23	Pasteur pipettes, 250 pcs	36590-00	1
24	Rubber caps, 10 pcs	39275-03	1
25	Spoon, special steel	33398-00	2
26	Wash bottle, plastic, 500 ml	33931-00	1
27	Citric acid 250 g	30063-25	1
28	Caustic soda solution, 1.0 m, 1000 ml	48329-70	1
29	Phenolphthalein, 0,5% soution in ethanol, 100 ml	31715-10	1
30	Activated carbon, granular 500 g	30011-50	1
31	Water, distilled 5 l	31246-81	1

Task

Determine the residual equilibrium concentrations of citric acid after stirring solutions of differing initial concentrations with a constant mass of activated carbon. Use the measurement results to determine which of the adsorption isotherms is valid for the given system.

Set-up and procedure
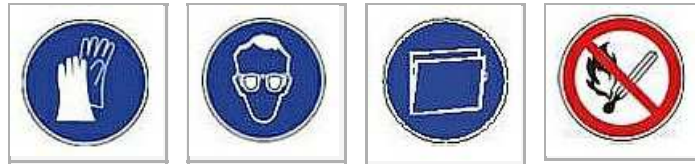
Set up the experiment as shown in Fig. 1. Prepare 1000 ml of 1.0 molar citric acid solution by dissolving 210.16 g of citric acid in distilled water and topping the volumetric flask off to the calibration mark. Pipette the volumes of this stock solution (V_{st}) that are listed in Table 1 into separate clean 250 ml volumetric flasks and top the flasks off to the calibration mark.
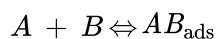
Pour 100 ml each of the six concentration series solutions into separate 250 ml Erlenmeyer flasks containing exactly 3.00 g of activated carbon. Slip a magnetic stirrer bar into each flask. Seal the flasks, then stir the solutions in them vigorously for approximately 30 minutes and filter them. Titrate the sample volumes V_1 of the respective filtrates, as given in Table 1, with 1.0 molar sodium hydroxide solution using phenolphthalein as indicator. Titrate 10 ml of the 1.0 molar citric acid stock solution V_0 similarly to check the initial concentration.
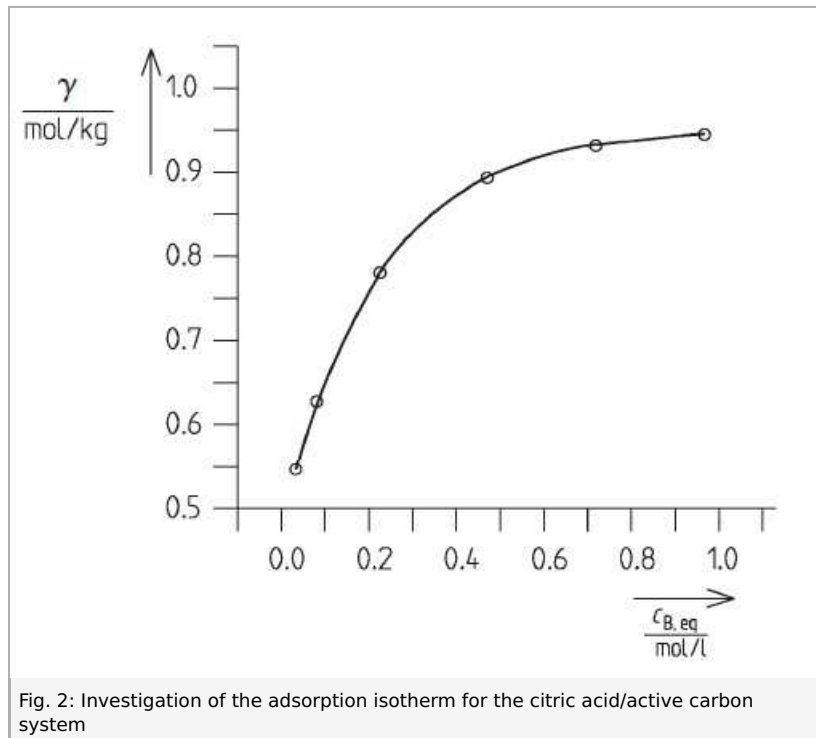
V_{st} / ml	V_1 / ml
250.0	10
187.5	10
125.0	25
62.5	25
25.0	50
12.5	50

- *Table 1*:
  Volumes of stock solution for the preparation of the concentration series V_{st} and the sample volumes after filtration V1 for the determination of the equilibrium concentration of citric acid.

Theory and evaluation

As a result of the action of attractive forces between exposed particles, gases or dissolved substances B attach themselves reversibly to the surfaces of solid phases A (adsorption).

$$A \: + \: B \Leftrightarrow AB_{\mathrm{ads}}$$

PHYWE excellence in science

Robert-Bosch-Breite 10
D - 37079 Göttingen

Tel: +49 551 604 - 0
Fax: +49 551 604 - 107

info@phywe.de
www.phywe.com

Fig. 2: Investigation of the adsorption isotherm for the citric acid/active carbon system

Type and strength of the interactions allow a differentiation to be made between physicosorption (weak van der Waals forces, very low adsorption enthalpies, a number of multilayers of the adsorbed substance) and chemisorption (chemical bonds, substantial adsorption enthalpies, monolayers of the adsorbed substance).

Adsorption and desorption represent an equilibrium, the position of which is temperature-dependent. Adsorption is accompanied by a decrease in surface tension and the liberation of heat of adsorption so that, acc. to Le Chatelier's principle for exothermic processes, adsorption must decrease with increasing temperature.

The quantity adsorbed is further dependent on the concentration of the substance in the contacting phase, and on the size of the adsorbing surface. As the value of the latter is very difficult to determine, however, the quantity of the substance adsorbed $n_{B,ads}$ is related to the mass of the adsorbent m_A which is proportional to the size of the adsorbing surface:

$$\gamma = \frac{n_{B,ads}}{m_A} \qquad (1)$$

Where

γ Adsorption molaltiy

The type and degree of adsorption are functions of the chemical nature of the adsorbent and the adsorbate as well as of the adsorbate temperature and concentration (for dissolved substances) or partial pressure (for gases). The correlation between the adsorption molality and the free equilibrium concentration of B at constant temperature is described by a number of adsorption isotherms.
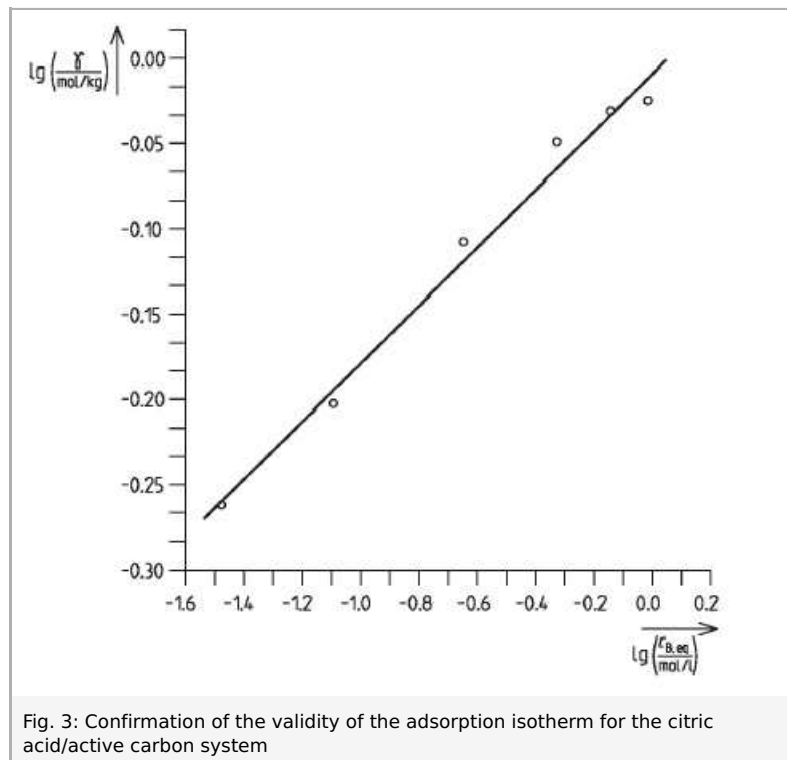
Freundlich empirically determined an adsorption isotherm in 1907:

$$\gamma = \alpha \cdot c_{B;eq}^{\beta} \qquad (2)$$

where

$c_{B;eq}$ Equilibrium concentration of B

α, β System-dependent constants

Fig. 3: Confirmation of the validity of the adsorption isotherm for the citric acid/active carbon system

The logarithmic expression of this

$$\lg\gamma = \lg c_{B;eq} + \lg a$$

(2.1)

allows simple graphic evaluation and thus the determination of the constants α and β (Fig. 3).

With increasing coverage of the surface, γ strives towards a limiting value γ_{max}, i.e. monolayer formation. The quotient of the real (γ) and the maximum (γ_{max}) adsorption molality is defined as the degree of coverage Θ.

$$\theta = \frac{\gamma}{\gamma_{max}}$$

(3)

Taking this into consideration, the adsorption isotherm can be derived by examining the kinetics of adsorption and desorption. The adsorption velocity is proportional to the product of the concentrations of the reaction partners, i.e. of the molecules of the adsorbate and the free positions on the surface of the adsorbent. When Θ represents the degree of coverage, then 1−Θ is the amount of free adsorbent surface.

$$-\frac{dc_B}{dt} = k_{ads}c_B(1-\theta) - k_{des}\theta$$

(4)

where

c_B Concentration of B in the solution

k_{ads}, k_{des} Rate constants of the adsorption and desorption, respectively

For the case of an established adsorption (-dc_B/dt = 0), Langmuir's adsorption isotherm follows (Fig. 2):

$$\gamma = \frac{\gamma_{max}Kc_{B,eq}}{1+Kc_{B,eq}}$$

(5)

where

$c_{B,eq}$ Equilibrium concentration of B in solution

K k_{ads}/k_{des} = constants

The correlation between adsorption molality and equilibrium concentration can be linearized by rearranging:

PHYWE excellence in science

Robert-Bosch-Breite 10
D - 37079 Göttingen

Tel: +49 551 604 - 0
Fax: +49 551 604 - 107

info@phywe.de
www.phywe.com

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\max} \cdot K} \cdot \frac{1}{c_{B,eq}} + \frac{1}{\gamma_{\max}}$$

(5.1)

In the region of the validity of the isotherm (5), the graphic plot of $1/\gamma$ as a function of the reciprocal equilibrium concentration $1/c_{B,eq}$ gives a straight line with a slope of $1/\gamma_{\max} K$ and the ordinate segment $1/\gamma_{\max}$.

With very low equilibrium concentrations ($K c_{B,eq} < 1$) the isotherm (5) simplifies to

$$\gamma = \gamma_{\max} K c_{B,eq} = K' c_{B,eq}$$

(5.2)

which is Henry-Dalton's law. Thus the adsorption molality γ is linearly correlated with $c_{B,eq}$.

In contrast, at very high equilibrium concentrations ($K c_{B,eq} > 1$), the adsorption molality tends toward a concentration independent limiting value $\gamma_{\max}$:

$$\gamma = \gamma_{\max}$$

(5.3)

To check which adsorption isotherms are valid in the investigated case, determine which expressions of adsorption molality (γ, $1/\gamma$, lg γ) correspond to relationships (5.2), (5.1) and (2.1) as functions of the corresponding equilibrium concentrations ($c_{B,eq}$, $1/c_{B,eq}$, lg $c_{B,eq}$).

The initial ($c_{B,0}$) and equilibrium concentration ($c_{B,eq}$) which are required for the evaluation can be calculated from the volume of the volumetric flask $V_K = 250$ ml and the volumes of NaOH of known concentration c_{NaOH} required to neutralise the sample volumes $V_{NaOH,0}$ and $V_{NaOH,1}$ of citric acid solution, taking the tribasicity of the absorbed material (citric acid) into account by applying the following relationships:

$$c_{B,0} = \frac{c_{NaOH} V_{NaOH,0} V_{st}}{3 V_0 V_K}$$

(6.1)

$$c_{B,eq} = \frac{c_{NaOH} V_{NaOH,1}}{3 V_1}$$

(6.2)

The adsorption molality γ can be determined from the following correlation, which is derived from equation (1)

$$\gamma = \frac{n_{B,ads}}{m_A} = \frac{(c_{B,0} - c_{B,eq}) \cdot V_s}{m_A}$$

(7)

where

$V_s = 100$ ml, system volume

$m_A = 3.00$ g = mass of adsorbent

Data and results

The linear correlation between the logarithms of the equilibrium concentration $c_{B,eq}$ and the adsorption molality γ demonstrated in Fig. 3 confirms the exclusive validity of Freundlich's adsorption isotherm in the investigated concentration range. The constant $\beta = 0.172$, which corresponds to the slope of the regression lines, lies in the range of values expected for granulated activated carbon ($0.1 < \beta < 1.0$).