Distribution equilibrium (Item No.: P3030701)

Curricular Relevance

Area of Expertise: Chemistry
Education Level: University
Topic: General Chemistry
Subtopic: Equilibria
Experiment: Distribution equilibrium

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

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

partial molar free enthalpy, chemical potential, equilibrium between phases, distribution and extraction, Nernst distribution equation, Lambert-Beer law, photometry

Overview

Short description

Principle

At constant temperature and under constant pressure, a dissolved substance distributes itself between two immiscible liquids in a constant concentration ratio. This ratio is equal to the partition coefficient (distribution coefficient) of the substance examined in the given two-phase system.

Fig. 1: Experimental set-up

Safety instructions

***trans*-Azobenzene**
H341: Suspected of causing genetic defects.
H350: May cause cancer.
P201: Obtain special instructions before use.
P273: Avoid release to the environment.
P314: Get medical advice/attention if you feel unwell.

Acetonitrile
H225: Highly flammable liquid and vapour.
H319: Causes serious eye irritation.
H332: Harmful if inhaled.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

***n*-Heptane**
H225: Highly flammable liquid and vapour.
H315: Causes skin irritation.
H410: Very toxic to aquatic life with long-lasting effects.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P273: Avoid release to the environment.
P331: Do NOT induce vomiting.

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	Trans-azobenzene f. synth., 100 g	31064-10	1
3	Separatory funnel 1000 ml	35850-04	1
4	Cell for spectrophotometer, optical glass	35664-00	2
5	Retort stand, h = 750 mm	37694-00	1
6	Acetonitrile 1000 ml	30000-70	1
7	Separatory funnel 250 ml pear-sh.	36884-00	4
8	Thermometer -10...+50 °C	38034-00	1
9	n-heptane, extra pure 250 ml	31366-25	1
10	Pipette dish	36589-00	1
11	Pipettor	36592-00	1
12	Erlenmeyer flask,narrow n.,1000ml	36122-00	1
13	Pasteur pipettes, 250 pcs	36590-00	1
14	Volumetric flask 250 ml, IGJ14/23	36550-00	1
15	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
16	Erlenmeyer flask,narrow n.,500 ml	36121-00	1
17	Volumetric flask 50 ml, IGJ12/21	36547-00	4
18	Support ring, i.d. 70mm,	37721-01	2
19	Right angle clamp	37697-00	2
20	Erlenmeyer flask,narrow n.,250 ml	36124-00	1
21	Volumetric pipette, 20 ml	36579-00	2
22	Glass beaker Boro, tall, 100 ml	46026-00	2
23	Rubber caps, 10 pcs	39275-03	1
24	Microspoon, steel	33393-00	1
25	Funnel, glass, top dia. 55 mm	34457-00	1
26	Volumetric pipette, 10 ml	36578-00	1
27	Wash bottle, plastic, 500 ml	33931-00	1
28	Rubber stopper,d=44/36mm,w/o hole	39262-00	1
29	Rubber stopper, d = 35 / 29 mm, without hole	39259-00	2

Task

Measure the extinction of various concentrated solutions of *trans*-azobenzene in acetonitrile at constant wavelength. Subsequently determine the equilibrium concentrations (extinctions) of *trans*-azobenzene in the system *n*-heptane/acetonitrile after single and repeated distribution at constant temperature. Calculate the partition coefficients and effectiveness of the extractions from the experimental data and compare them.

Set-up and procedure

The spectrophotometer that is required for this experiment is shown in Fig. 1.

Acetonitrile saturated with *n*-heptane, and *n*-heptane saturated with acetonitrile are required for this experiment. Prepare them as follows: Pour about 500 ml of acetonitrile and 200 ml of *n*-heptane into a 1000 ml Erlenmeyer flask and shake vigorously (*Caution!* Equalize pressure!). Allow the flask to stand for some time, with vigorous shaking now and again. Use a separating funnel to cleanly separate the saturated acetonitrile so prepared from the saturated *n*-heptane, and store each of them in separate, appropriately labeled Erlenmeyer flasks.

Directly prior to measurement, weigh 75 mg ($4.12 \cdot 10^{-4}$ mol) of *trans*-azobenzene into a 250 ml volumetric flask and dissolve it in heptane-saturated acetonitrile (fill up to the calibration mark). Prepare dilutions from this $1.65 \cdot 10^{-3}$ molar stock solution as follows: Pipette 10, 20, 30 and 40 ml of the solution each into a separate 50 ml volumetric flask, then fill each of these four flasks up to the 50 ml mark with heptane-saturated acetonitrile.

Measure and record the extinctions of the stock solution and the dilution series at 400 nm, 420 nm and 440 nm, using heptanesaturated acetonitrile as reference in each case. Plot a graph of the measured values (see Fig. 2).

Carry out the subsequent examinations of the distribution of *trans*-azobenzene in the prescribed *n*-heptane/acetonitrile two phase system as follows:

a) Single distribution

Pipette exactly 60 ml of the $1.65 \cdot 10^{-3}$ molar stock solution of *trans*-azobenzene in acetonitrile into a clean, dry separating funnel and cover it with 60 ml of acetonitrile-saturated n-heptane. Shake vigorously for about 10 minutes (*Caution!* Equalize pressure!). When the phases have separated, run off the lower phase and measure the extinction of it at the same wavelengths as previously (400 nm, 420 nm and 440 nm) against heptane-saturated acetonitrile. The upper phase is not required, discard it by pouring it into the container for organic solvent waste disposal.

b) Repeated distribution

Pipette exactly 60 ml of the stock solution into a clean and dry separating funnel and add to it 20 ml of acetonitrile-saturated *n*-heptane. Shake as described above (*Caution!* Equalize pressure!). When the phases have separated, run the lower phase quantitatively off into a second clean, dry separating funnel. Again cover it with 20 ml of acetonitrile-saturated n-heptane and extract as above. Discard the upper hexane phase as required by waste disposal regulations. Repeat this last extraction in a further separating funnel with a fresh 20 ml of acetonitrile-saturated *n*-heptane. In this way, a total of 6 ml has again been used for extraction. Separate off the lower phase and measure the extinction of it at the same wavelengths as previously with single distribution (400 nm, 420 nm and 440 nm) against heptane- saturated acetonitrile.

The spectra of *trans*-azobenzene in acetonitrile before and after single and repeated distribution can be additionally recorded. To do this, measure the extinction of each of the three solutions against heptane-saturated acetonitrile in the range from 360 to 550 nm and steps of 5 nm, and plot the measured values as shown in Fig 3. This is not absolutely necessary for the measurement and evaluation, however.

Note: Fresh solutions of *trans*-azobenzene are to be used, and work with them is to be carried out briskly, as it is not very stable in organic solvents (this is shown by changes in the spectroscopic behaviour, within as little as a few hours the spectra are no longer reproducible!).

Theory and evaluation

When a solvent 1, in which a substance A is dissolved, is brought into contact with a liquid 2, that is immiscible with solvent 1, then because of:

$$\mu_{\mathrm{A},1} > \mu_{\mathrm{A},2} \quad (1)$$

$$\mu^0_{\mathrm{A},1} + RT\ln a_{\mathrm{A},1} > \mu^0_{\mathrm{A},2} + RT\ln a_{\mathrm{A},2} \quad (1.1)$$

where

$\mu_{\mathrm{A},1}$, $\mu^0_{\mathrm{A},1}$; $\mu_{\mathrm{A},2}$, $\mu^0_{\mathrm{A},2}$ Chemical potential (μ) or chemical standard potential (μ^0) of the substance A in the phases 1 and 2

$a_{\mathrm{A},1}$, $a_{\mathrm{A},2}$ Activities of the substance A dissolved in solvent 1 or 2

R Universal gas constant

T Temperature

a spontaneous transfer of substance into the unoccupied phase 2 takes place up to equalization of the difference in potentials. The following is valid in the resulting distribution equilibrium:

$$\mu_{\mathrm{A},1} = \mu_{\mathrm{A},2} \quad (2)$$

$$\mu^0_{\mathrm{A},1} + RT\ln a_{\mathrm{A},1} = \mu^0_{\mathrm{A},2} + RT\ln a_{\mathrm{A},2} \quad (2.1)$$

from which

$$\frac{\mu^0_{\mathrm{A},1} - \mu^0_{\mathrm{A},2}}{RT} = \ln\frac{a_{\mathrm{A},2}}{a_{\mathrm{A},1}} = \mathrm{const.} \quad (2.2)$$

and so

$$\frac{a_{\mathrm{A},2}}{a_{\mathrm{A},1}} = k_{\mathrm{N}} \quad (3)$$

follows. According to the Nernst distribution law that is expressed in equation (3), the ratio of the activities a_{A} (or concentrations c_{A} on strong dilution) of a substance A that is distributed between two co-existing phases at a given pressure p and a given temperature T is constant and equal to the Nernst partition coefficient k_{N} (distribution constant). This is in the ideal case (no intermolecular effects, substance A is present in the same form in the two phases) independent of the amount of distributed substance. It is determined by the nature of the substance A, the type of two-phase system and the temperature. The temperature dependence can be neglected in practice because of the low distribution enthalpies, so that work can be carried out at room temperature without the need for thermostatting. It is clear that normally the phase positioned in the numerator in definition (3) is the liquid of lowest density (upper phase).

To calculate the partition coefficient acc. to (3), the equilibrium concentrations of substance A in the two phases must be known. Because of (3.1), however, measurements on one phase (the experimentally most easily handled one) are sufficient.

$$k_{\mathrm{N}} = \frac{c_{\mathrm{A},2}}{c_{\mathrm{A},1}} = \frac{n^{(0)}_{\mathrm{A},1} - n_{\mathrm{A},1}}{n_{\mathrm{A},1}} \cdot \frac{V_1}{V_2} = \frac{c^{(0)}_{\mathrm{A},1} - c_{\mathrm{A},1}}{c_{\mathrm{A},1}} \cdot \frac{1}{V} \quad (3.1)$$

where:

$n^{(0)}_{\mathrm{A},1}$, $n_{\mathrm{A},1}$ Initial quantity ($n^{(0)}$) or equilibrium quantity (n) of A in phase 1. The constant volume of the lower phase allows conversion to the initial concentration $c^{(0)}_{\mathrm{A},1}$ or the equilibrium concentration $c_{\mathrm{A},1}$ to be made.

$V = V_2/V_1$ Volume ratio of the two phases

Rearranging relationship (3.1) for $c_{\mathrm{A},1}$, we obtain:

$$c_{\mathrm{A},1} = \frac{c^{(0)}_{\mathrm{A},1}}{1 + k_{\mathrm{N}}V} \quad (3.2)$$

The value of this is, in contrast to the partition coefficient, dependent on the experimental procedure. When, alternatively to single distribution, pure upper phase is not added as a total volume, but in several portions for repeated distribution, then analogously to (3.2) we have $c^{(1)}_{A,1}$ for the equilibrium concentration after the first distribution, or extraction, step:

$$c^{(1)}_{A,1} = \frac{c^{(0)}_{A,1}}{1+k_N V} \tag{3.2.1}$$

The concentration remaining in the lower phase after the second distribution step is given when, in (3.2.1), $c^{(0)}_{A,1}$ is replaced by $c^{(1)}_{A,1}$ and $c^{(1)}_{A,1}$ by $c^{(2)}_{A,1}$:

$$c^{(2)}_{A,1} = \frac{c^{(1)}_{A,1}}{1+k_N V} = \frac{c^{(0)}_{A,1}}{(1+k_N V)^2} \tag{3.2.2}$$

Correspondingly, after *n* distribution steps:

$$c^{(n)}_{A,1} = \frac{c^{(0)}_{A,1}}{(1+k_N V)^n} \tag{3.2.3}$$

According to this relationship, the concentration of the substance A remaining in the lower phase falls with the number of distribution steps, which allows consequences to be drawn for the practical procedure. The quotient of the equilibrium concentration and initial concentration is so a measure of the quality of the extraction and is named the effectiveness of extraction φ .

$$\varphi = \frac{c^{(n)}_{A,1}}{c^{(0)}_{A,1}} \tag{4}$$

The determination of the concentration of colored or UV active compounds can be carried out photometrically on the basis of the Lambert-Beer law:

$$E_\lambda = \varepsilon_A c_A d \tag{5}$$

where

E_λ Extinction at a wavelength of λ

ε_A Decadic molar extinction coefficient of substance A at a wavelength of λ

c_A Concentration of substance A in mol/l

d Layer thickness in the cell

The validity of this must be experimentally substantiated for the system to be examined (Fig. 2). The extinction values measured before and after distribution can be assigned concentration values from the calibration curves obtained at various wavelengths (Fig. 2) or the corresponding mathematical connections. Alternatively, when there is a proven linear relationship between *E* and c_A , the extinction values measured for the lower phase before (E_0) and after single (E_1) or repeated (E_n) distribution can be used directly in equations (3.1). (3.2.3) and (4) in place of the concentrations, whereby the following changes in the k_N or φ explicit connections can also be made:

$$k_N = \frac{E_0 - E_1}{E_1} \cdot \frac{1}{V} \tag{6}$$

$$k_N = \frac{\sqrt[n]{\frac{E_0}{E_n}} - 1}{V} \tag{7}$$

$$\varphi = \frac{E_n}{E_0} \tag{8}$$

Robert-Bosch-Breite 10
D - 37079 Göttingen

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

info@phywe.de
www.phywe.com

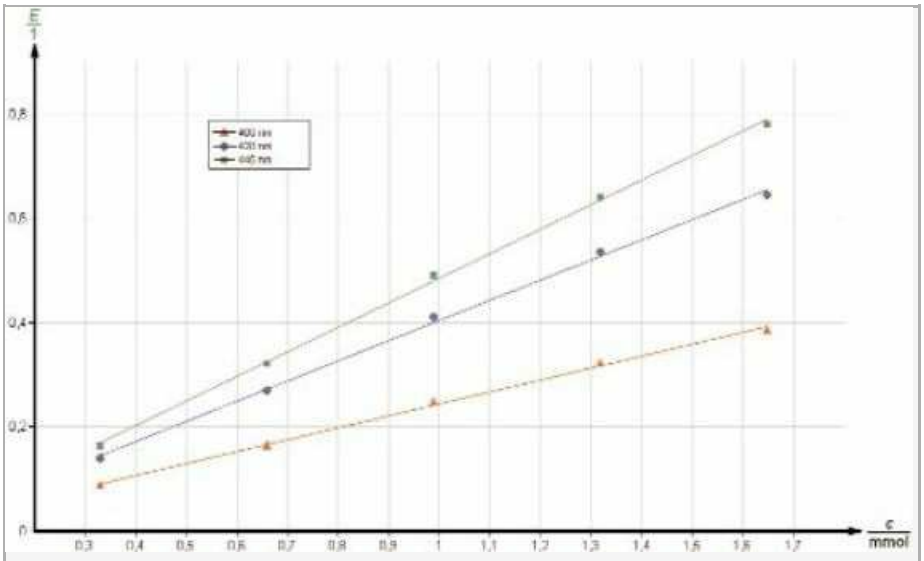

Fig. 2: The relationship between extinction E and concentration cA for trans-azobenzene in acetonitrile at λ = 400 mm (Δ), λ = 420 mm (O) and λ = 440 nm (□) (proof of the validity of the Lambert-Beer law).

Data and results

Fig. 3 shows the ranges of the VIS spectra of trans-azobenzene in acetonitrile recorded before and after single and repeated distribution at T = 299 K.

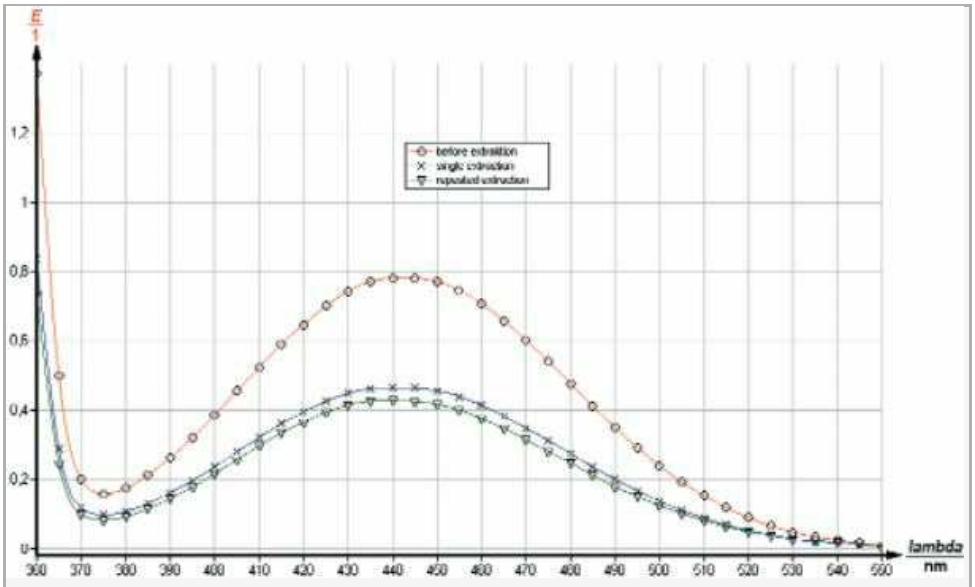

Fig. 3: Segment of the VIS spectrum of *trans*-azobenzene in acetonitrile before (O) and after single (X) and repeated (▽) extraction with the same total volume of *n*-heptane at T= 299 K.

The extinctions of the marked absorption bands at λ= 400 nm can be read off from these spectra: E_0 = 0.385 (before distribution), E_1 = 0.236 (after single distribution) and E_3 = 0.216 (after repeated distribution). Together with relationship (6) or (7), a partition coefficient of k_N = 0.631 is obtained for E_1 with V= 1 and n= 1 (single distribution) and, with relationship (7), an approximately equal value of k_N = 0.637 for E_3 with V= 1/3 and n= 3 (repeated distribution).

k_N = 0.647 was the average value obtained from several calculations at various wavelengths in the proximity of maximum absorption.

As a comparison, the concentration ratios calculated for E_3 and E_1 using equation (8) give φ_3 = 0.570 (for repeated distribution) compared to φ_1 = 0.620 (for single distribution), which do not indicate a substantially greater reduction in *trans*-azobenzene in the lower phase by repeated distribution with the same total volume of extraction solvent (*n*-heptane).

For preparative extraction purposes, therefore, the two-phase system used here should be replaced by a system with a higher partition coefficient, and so greater extraction effectiveness.

Note

The graphical evaluation of the measured values can be very easily carried out by means of “Measure” software. A download file of this software is available as freeware for use in evaluating and graphically representing measured values under URL www.phywe.com. Figs. 2 and 3 were created by this software.

Robert-Bosch-Breite 10
D - 37079 Göttingen

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

info@phywe.de
www.phywe.com