

Diffusion - Determination of Diffusion Constants using the Schlieren Method

Protocol for the PC 2 lab course by
Vincent Kümmerle & Elvis Gnaglo & Julian Brügger

University of Stuttgart

authors: Vincent Kümmerle, 3712667
st187541@stud.uni-stuttgart.de

Elvis Gnaglo, 3710504
st189318@stud.uni-stuttgart.de

Julian Brügger, 3715444
st190050@stud.uni-stuttgart.de

group number: A05

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supervisor: Xiangyin Tan

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Abstract: In this experiment the diffusion constants of the salts NaCl, KCl and ZnSO₄ were determined by using the Schlieren method. The calculated diffusion constants were $D_{\text{NaCl}} = 1.414 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{KCl}} = 6.636 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{ZnSO}_4} = 2.925 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

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1 Theory

Molecular diffusion describes the movement of particles from a region of high concentration to a region of low concentration, which leads to an even distribution of particles.^[1] It was first discovered by Robert Brown, who observed the random movement of tiny particles suspended in a liquid, which is called Brownian motion. Then German physicist Adolf Fick lay the theoretical foundation for diffusion by formulating two laws.

The first Fick's law describes how the particle flux density $j(z)$ is connected to the Diffusion coefficient D and the concentration gradient $\frac{\partial c(z)}{\partial z}$, which is shown in Equation 1.

$$j(z) = -D \cdot \frac{\partial c}{\partial z} \quad (1)$$

The physical meaning of the first Fick's law is that a concentration gradient leads to mutual diffusion of particles, leading to an even distribution. The diffusion coefficient can also be defined by the „Einstein relation“ in Equation 2.

$$D = \frac{1}{2} \nu \Delta z^2 \quad (2)$$

ν is the jump rate and Δz^2 the mean square jump distance of particles, assuming that they can only move along the z axis. Second Fick's law describes the temporal course of concentration as shown in Equation 3.

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial z^2} \quad (3)$$

Equation 3 states that the concentration equalization proceeds faster the stronger the concentration gradient. By integrating second Fick's law from Equation 3 under certain boundary conditions and using the substitution $\mu = \frac{z}{\sqrt{4Dt}}$, Equation 4 for the profile of concentration can be obtained.

$$c = \frac{c_2}{2} \cdot \left(1 - \frac{2}{\sqrt{\pi}} \int_0^\mu e^{-\mu^2} d\mu \right) \quad (4)$$

By deriving Equation 4, the function is simplified into Equation 5 which leads to the concentration gradient profile having the shape of a Gaussian bell curve, as is illustrated in Figure 1.

$$\frac{dc}{dz} = -\frac{c_2}{2\sqrt{\pi Dt}} \cdot e^{-\mu^2} \quad (5)$$

Assuming that the refractive index n is proportional to c and knowing that the gradient has an extreme value at $z = 0$, as can be seen in Figure 1, Equation 6 describes the refractive index gradient at $z = 0$ with the indices of water n_1 and of the salt solution n_2 .^[1]

$$\left(\frac{dn}{dz} \right)_{z=0} = -\frac{n_1 - n_2}{2\sqrt{\pi Dt}} \quad (6)$$

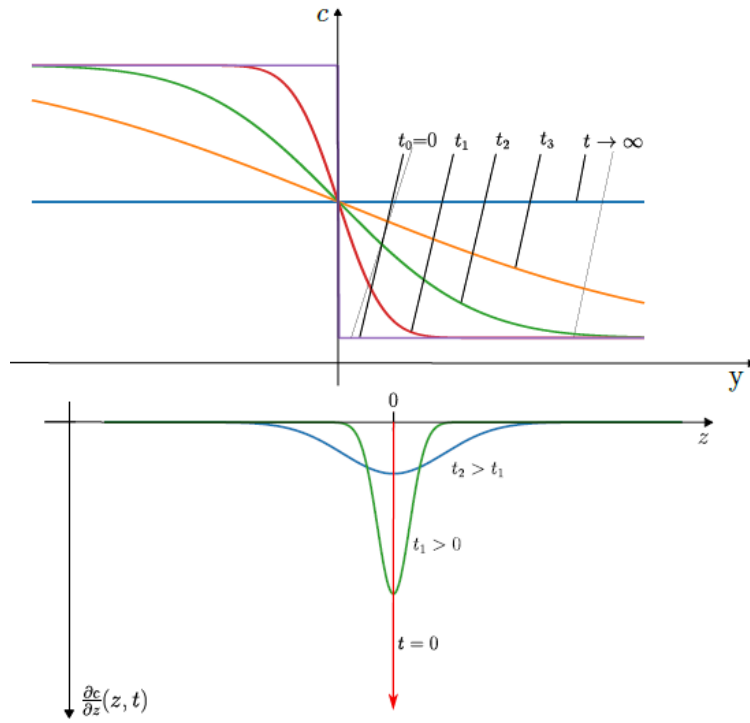


Figure 1: Profiles of the concentration and concentration gradient.^[1]

Following this argumentation, diffusion leads to a continuously changing refractive index profile which causes a light beam directed to a cuvette of a salt solution with a concentration gradient to be refracted toward the optically denser medium. That is called Snell's law of refraction and shown in Figure 2. The exit angle β and the degree of curvature can be described with Equation 7 and 8, where α is the angle of incidence and r the radius of the curvature of the light beam.^[1]

$$\beta = \frac{n}{n_0} \alpha \quad (7)$$

$$\frac{1}{r} = \frac{1}{n} \frac{dn}{dz} = \frac{d \ln(n)}{dz} \quad (8)$$

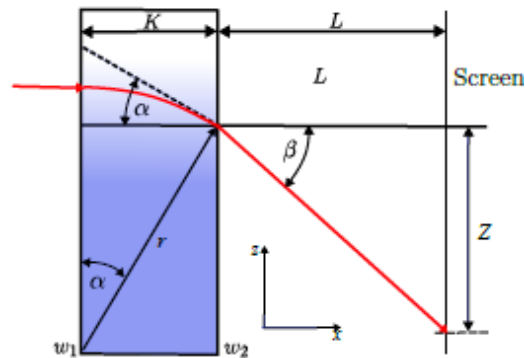


Figure 2: Scheme of the experimental setup geometry.^[1]

The Huygen's principle states that every point of a wavefront can be seen as the origin of a spherical elementary wave. That's why the path of the light beam is curved in a medium with a spatially dependent refractive index $n(z)$ due to a lateral phase shift within the wavefront. The strongest deflection is experienced by the part of the beam that passes through the steepest concentration gradient region. With the small-angle approximation and Equation 7 and 8, the refractive index gradient can be described by Equation 9.

$$\frac{dn}{dz} \approx \frac{Z}{L} \cdot \frac{n_0}{K} \quad (9)$$

L is the distance between the cuvette and the screen, K the thickness of the cuvette, n_0 the refractive index of air and Z the distance between the straight extension of the beam at the exit point and the impact point on the screen. By equating Equation 9 and Equation 6 and rearranging to the diffusion constant D , Equation 10 is derived to calculate D using the Schlieren Method.^[1]

$$D = \frac{(n_1 - n_2)^2 L^2 K^2}{4\pi n_0^2 Z^2 t} \quad (10)$$

2 Procedure

The experimental setup was already built prior to the start of the measurements as shown in Figure 2. The laser beam light path was tilted at about 45°.

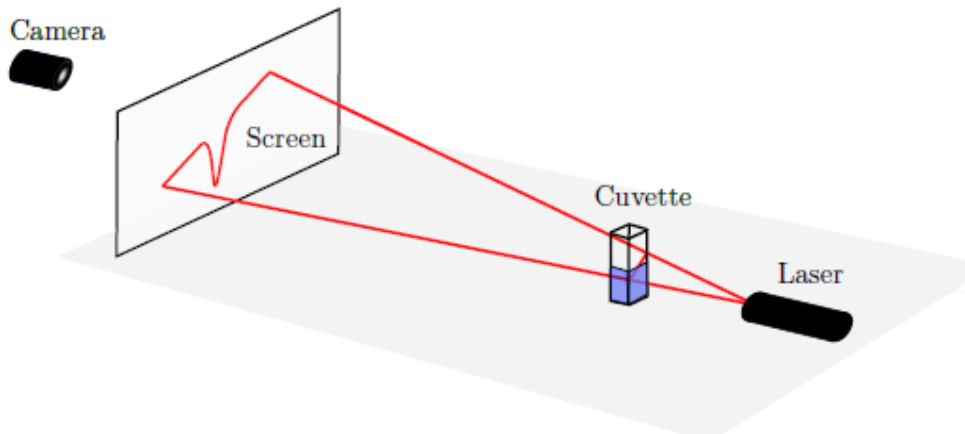


Figure 3: Scheme of the laser beam geometry.^[1]

The experiment began by doing a calibration measurement where the settings of the camera were adjusted, so that the only visible part was the laser beam. Afterwards the cuvette was half filled with deionized water and underlayered with a 2 molar solution of sodium chloride. As soon as the sodium chloride solution was underlayered the video recording was started. After 15 minutes the recording was stopped the resulting video was analyzed by taking snapshots at relevant timestamps. Those snapshots were uploaded into the python skript "convert-image.py" which converted

the snapshots into xy-value pairs. The resulting ".dat" file was then uploaded into the python skript "auswertung diffusion.py" where the amplitude was determined by adjusting slider. These steps were repeated for the 2 molar potassium chloride and zinc sulfate solutions. The potassium chloride solution was also recorded for 15 minutes and the zinc sulfate solution was recorded for 30 minutes. During the recording of the sodium chloride solution the refracting indices of deionized water, and the three solutions were measured using a refractometer.

3 Analysis

3.1 Refractive indices

The refractive indices of deionized water and the different salt solutions were measured with a refractometer and are listed in Table 1.

Table 1: Measured refractive indices of deionized water and different salt solutions.

Solution	n
H ₂ O (deionized)	1.3375
NaCl (2M)	1.3541
KCl (2M)	1.3514
ZnSO ₄ (2M)	1.3725

The NaCl and KCl solutions have similar refractive indices of $n_{\text{NaCl}} = 1.3541$ and $n_{\text{KCl}} = 1.3514$, while the ZnSO₄ solution has a significantly higher refractive index of $n_{\text{ZnSO}_4} = 1.3725$ than the others. This is due to the much higher polarizability of the larger SO₄²⁻ ion with a higher ionic charge in comparison to the Cl⁻ ion. Additionally, the higher molar mass of ZnSO₄ results in a significantly higher mass density at the same molar concentration (2M). Na⁺ has a higher charge density than K⁺ due to its smaller size, which polarizes the surrounding water molecules more, leading to a slightly higher refractive index.

3.2 Diffusion coefficients

In order to determine the diffusion coefficients, the pixel value from the graphs has to be converted into a real length, using an appropriate conversion factor F , that is defined as:

$$F = 0,139 \text{ mm/pixel} \quad (11)$$

To evaluate Figure 5, Equation 10 is rearranged to Z^{-2} to get Equation 13, which

shows the connection between the slope m and the diffusion coefficient.

$$Z^{-2} = \frac{4\pi D n_0^2}{(n_1 - n_2)^2 L^2 K^2} \cdot t \quad (12)$$

$$= m \cdot t \quad (13)$$

3.2.1 NaCl

Figure 4 shows the picture of the laserbeam on the screen plotted and quantified in pixels.

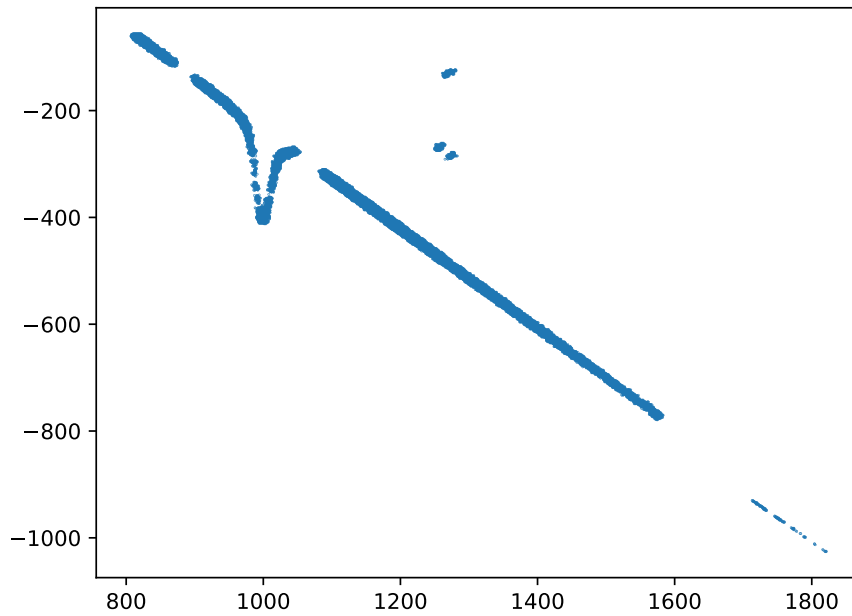


Figure 4: The screenshot after 30s of NaCl, plotted in pixels.

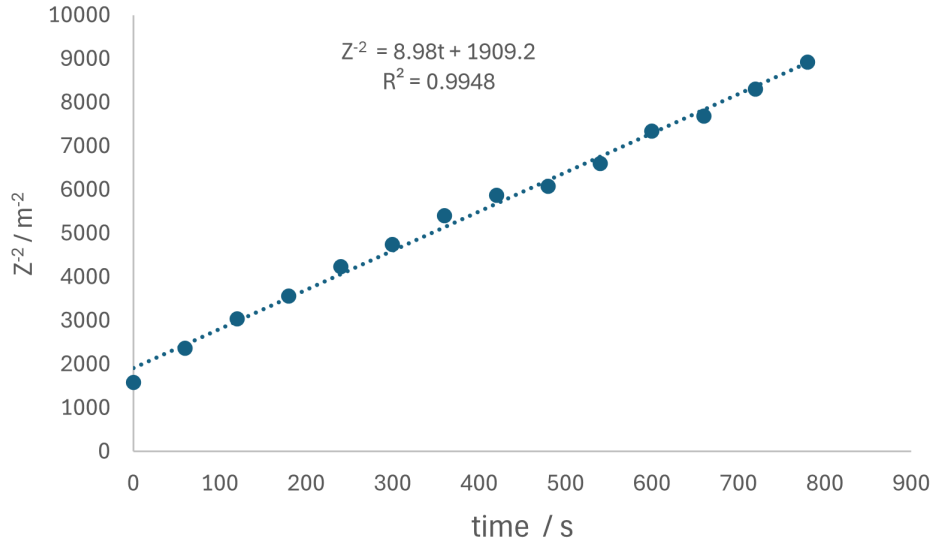
The depth of the amplitude $Z_{m,\text{NaCl}}$ was determined via python and converted into a real length using Equation 11

$$Z_{m,\text{NaCl},10s} = \Delta y_{p,\text{NaCl},10s} \cdot F = 147.7 \text{ pixels} \cdot 0,139 \text{ mm/pixel} = 20,5 \text{ mm} = 0,0205 \text{ m}$$

$Z_{m,\text{NaCl}}$ is calculated for every screenshot that was made in a 60 s time interval over the course of a 15 min video. To determine the fusion coefficient D the amplitude $Z_{m,\text{NaCl}}$ negative squared is plotted over the time t as shown in Figure 5 The values, that were used for the plot are listet in Table 2

Table 2: Measured values of Δy , Z , and Z^{-2} as a function of time of the NaCl-Sample

Time [s]	Δy	Z [mm]	z [m]	z^{-2} [m ⁻²]
0	180.6246	25.1068	0.0251068	1586.4143
60	147.7368	20.5354	0.0205354	2371.3348
120	130.5184	18.1421	0.0181421	3038.2730
180	120.4435	16.7416	0.0167416	3567.8270
240	110.5652	15.3686	0.0153686	4233.8307
300	104.4336	14.5163	0.0145163	4745.5833
360	97.8275	13.5980	0.0135980	5408.1442
420	93.8439	13.0443	0.0130443	5877.0411
480	92.2600	12.8241	0.0128241	6080.5605
540	88.5696	12.3112	0.0123112	6597.8315
600	83.9791	11.6731	0.0116731	7338.8412
660	82.0591	11.4062	0.0114062	7686.2952
720	78.9158	10.9693	0.0109693	8310.7991
780	76.1865	10.5899	0.0105899	8916.9066

Figure 5: The values of the negative squared Amplitude $Z_{m,\text{NaCl}}$ plotted over the time t

The linear fit is described by the equation

$$y = m \cdot t + b,$$

where the slope is $m = 8.98 \text{ m}^{-2} \text{ s}^{-1}$ and the intercept is $b = 1909.2 \text{ m}^{-2}$. The slope of the line is defined as

$$m = \frac{4\pi D n_0^2}{(n_1 - n_2)^2 L^2 K^2}. \quad (13)$$

The parameters are given as $K = 0.01$ m, $L = 0.268$ m, $n_{2,\text{NaCl}} = 1.3541$, $n_1 = 1.3375$, and $n_0 = 1$. Using the experimentally determined slope, the diffusion coefficient of sodium chloride can be calculated as

$$D_{\text{NaCl}} = \frac{(n_1 - n_2)^2 L^2 K^2 m}{4\pi n_0^2}. \quad (14)$$

Substituting the numerical values yields

$$D_{\text{NaCl}} = \frac{(1.3541 - 1.3375)^2 (0.268 \text{ m})^2 (0.01 \text{ m})^2 \cdot 8.98 \text{ m}^{-2} \text{ s}^{-1}}{4\pi} = 1.414 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}. \quad (15)$$

3.2.2 KCl

The same steps that were discussed for the NaCl sample were performed on the values of the KCl sample. The values are listed in Table 3 and plotted in Figure 6

Table 3: Measured values of Δy , Z , and Z^{-2} as a function of time of the KCl-Sample

Time [s]	Δy	Z [mm]	z [m]	z^{-2} [m ⁻²]
0	112.4616	15.6322	0.0156322	4092.2471
30	102.6179	14.2639	0.0142639	4915.0055
60	97.1659	13.5061	0.0135061	5482.0507
90	87.6999	12.1903	0.0121903	6729.3335
120	84.9633	11.8099	0.0118099	7169.8102
150	82.4873	11.4657	0.0114657	7606.6941
180	76.0766	10.5747	0.0105747	8942.6829
210	73.8591	10.2664	0.0102664	9487.7385
240	71.1075	9.8839	0.0098839	10236.2241
270	68.7144	9.5513	0.0095513	10961.6230
300	69.5558	9.6683	0.0096683	10698.0225
330	64.5744	8.9758	0.0089758	12412.2252
360	65.9762	9.1707	0.0091707	11890.3701
420	59.6900	8.2969	0.0082969	14526.7050
480	57.6158	8.0086	0.0080086	15591.4610
540	56.1047	7.7986	0.0077986	16442.6631
600	51.5612	7.1670	0.0071670	19468.1697
660	50.4075	7.0066	0.0070066	20369.5227
720	47.8183	6.6467	0.0066467	22635.0895
780	47.2975	6.5744	0.0065744	23136.2613
840	45.0385	6.2604	0.0062604	25515.3842
900	41.4357	5.7596	0.0057596	30145.3490

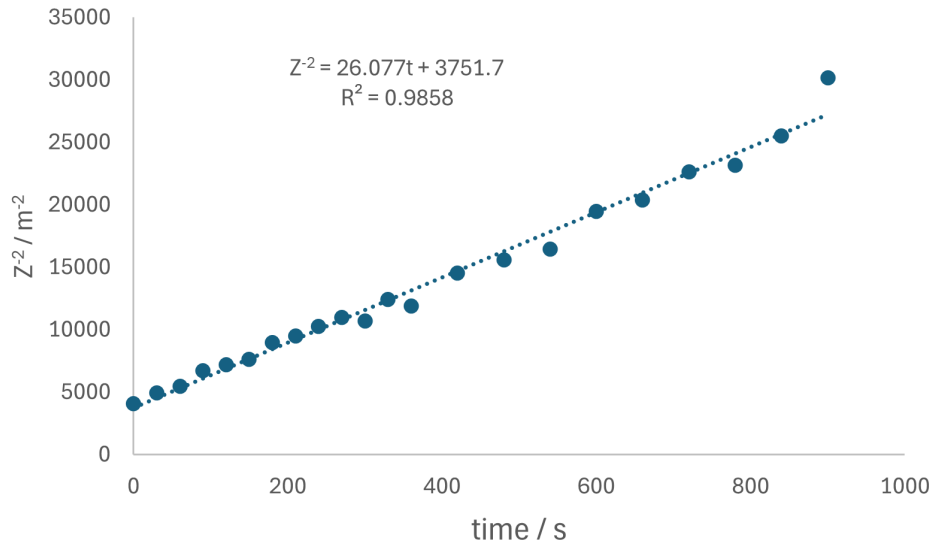


Figure 6: The values of the negative squared Amplitude $Z_{m,\text{KCl}}$ plotted over the time t

The slope m is determined to be

$$m = 26.077 \text{ m}^{-2} \text{ s}^{-1},$$

and the refractive index of the potassium chloride solution is

$$n_{1,\text{KCl}} = 1.3514.$$

Using these values, the diffusion coefficient of potassium chloride can be calculated according to the corresponding relation, yielding

$$D_{\text{KCl}} = 6.636 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}.$$

3.2.3 ZnSO_4

The same steps that were discussed for the NaCl sample were also performed on the values of the ZnSO_4 sample. The Values are listet in Table 4 and plottet in Figure 7

Table 4: Measured values of Δy , Z , and Z^{-2} as a function of time of the ZnSO_4 -Sample

Time [s]	Δy	Z [mm]	z [m]	z^{-2} [m ⁻²]
0	262.6980	36.5150	0.0365150	749.9926
30	255.8125	35.5579	0.0355579	790.9096
60	252.3181	35.0722	0.0350722	812.9684
90	249.4520	34.6738	0.0346738	831.7567
120	245.3143	34.0987	0.0340987	860.0517
150	239.1358	33.2399	0.0332399	905.0679
180	233.1782	32.4118	0.0324118	951.9068
210	233.4213	32.4456	0.0324456	949.9256
240	402.7826	55.9868	0.0559868	319.0282
270	428.8795	59.6142	0.0596142	281.3843
300	438.3061	60.9245	0.0609245	269.4110
330	416.0718	57.8340	0.0578340	298.9743
360	464.4842	64.5633	0.0645633	239.8990
390	460.6664	64.0326	0.0640326	243.8918
420	458.9758	63.7976	0.0637976	245.6919
480	469.9451	65.3224	0.0653224	234.3560
540	463.5952	64.4397	0.0644397	240.8200
600	446.6395	62.0829	0.0620829	259.4514
660	446.3221	62.0388	0.0620388	259.8206
720	420.6900	58.4759	0.0584759	292.4463
780	413.1437	57.4270	0.0574270	303.2272
840	407.4944	56.6417	0.0566417	311.6930
900	398.9835	55.4587	0.0554587	325.1326
960	381.3652	53.0098	0.0530098	355.8675
1020	370.0731	51.4402	0.0514402	377.9162
1080	361.5875	50.2607	0.0502607	395.8619
1140	345.6014	48.0386	0.0480386	433.3307
1200	334.4851	46.4934	0.0464934	462.6118
1260	323.1864	44.9229	0.0449229	495.5234
1320	312.7687	43.4749	0.0434749	529.0829
1380	302.8585	42.0973	0.0420973	564.2749
1440	292.1175	40.6043	0.0406043	606.5340
1500	283.4248	39.3960	0.0393960	644.3097
1560	284.1040	39.4905	0.0394905	641.2327
1620	277.0211	38.5059	0.0385059	674.4420
1680	272.4736	37.8738	0.0378738	697.1425
1740	267.4768	37.1793	0.0371793	723.4329
1800	229.0740	31.8413	0.0318413	986.3223

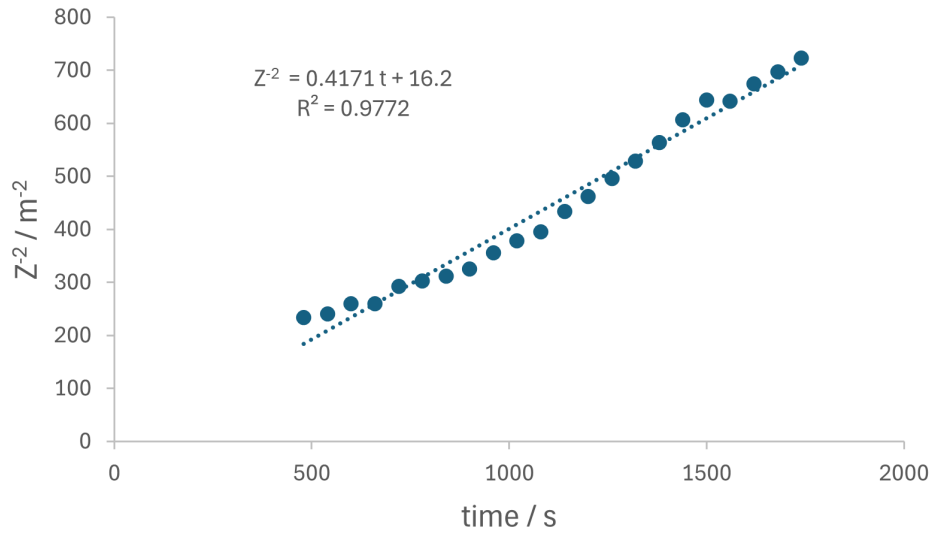


Figure 7: The values of the negative squared Amplitude Z_{m,ZnSO_4} plotted over the time t

Due to poor linearity during the first 540 s, the data from this interval is ignored in the plot. Nevertheless, even without that time period the correlation coefficient shows the lowest of the three accuracies.

The slope m is determined to be

$$m = 0.4171 \text{ m}^{-2} \text{ s}^{-1},$$

and the refractive index of the potassium chloride solution is

$$n_{1,\text{KCl}} = 1.3725.$$

Using these values, the diffusion coefficient of potassium chloride can be calculated according to the corresponding relation, yielding

$$D_{\text{ZnSO}_4} = 2.925 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}.$$

4 Error Discussion

There were multiple sources for errors in this experiment that have to be considered. The refractive indices of the salt solutions deviate from literature values due to manual adjustment of the borderline in the refractometer, which was based on subjective visual inspection. Especially in the case of ZnSO_4 , the borderline was very blurry, which led to a measurement uncertainty in the refractive index. The measurements of the refractive indices were performed at room temperature without active thermal stabilization, which can lead to deviations as well, since refractive indices are temperature dependent. The measured refractive indices were $n_{\text{H}_2\text{O}} = 1.3375$, $n_{\text{NaCl}} = 1.3541$, $n_{\text{KCl}} = 1.3514$ and $n_{\text{ZnSO}_4} = 1.3725$, while the literature values were $n_{\text{H}_2\text{O},\text{Lit}} = 1.333^{[2]}$, $n_{\text{NaCl},\text{Lit}} = 1.348^{[3]}$, $n_{\text{KCl},\text{Lit}} = 1.352^{[4]}$ and $n_{\text{ZnSO}_4,\text{Lit}} = 1.36^{[5]}$

Another possible source for errors was the lamp that was used to measure the refractive indices, since the different wavelengths of light are refracted differently. The adding of the salt solutions in the cuvette is also a source for errors because the two layers started mixing during the injection process of the salt solution if it was not done careful enough.

The measured diffusion constants $D_{\text{NaCl}} = 1.414 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{KCl}} = 6.636 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{ZnSO}_4} = 2.925 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ deviate from the ones obtained from literature sources which were $D_{\text{NaCl},\text{Lit}} = 1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{KCl},\text{Lit}} = 1.95 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{ZnSO}_4,\text{Lit}} = 1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.^[6]

The last possible error source was the recording process and the following conversion into data points. The brightness in the recording could have been too low for the python skript to be able to convert properly, which leads to missing points in the resulting plot. Additionally the conversion from pixels into millimeters relies on the assumption that the distance between the screen and camera is the exact distance as stated in the instruction. It is assumed that at a concentration of 2M, the refractive index is still proportional to the concentration. However, at higher concentrations, deviations can occur due to strong Coulomb interactions between multivalent ions such as ZnSO_4 , which lead to the formation of ion pairs and an electrostriction effect. This results in a higher density of the solution and a higher molar refractivity than expected, contributing to a deviation of the linear relationship between refractive index and concentration. The influence of deviations in the refractive indices on the diffusion coefficients calculated with Equation 10 is significant, since the refractive indices appear squared in the denominator.^[6]

5 Conclusion

The diffusion constants of NaCl, KCl and ZnSO_4 were determined as $D_{\text{NaCl}} = 1.414 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{KCl}} = 6.636 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{ZnSO}_4} = 2.925 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ by using the schlieren method. Most deviations from literature values can be explained by mistakes during the conduction of the experiment or errors in the setup.

6 References

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