

# 2010年臺灣國際科學展覽會 優勝作品專輯

編號：140013

## 作品名稱

簡易方法測量擴散係數

## 得獎獎項

物理與太空科學科大會獎一等獎

美國正選代表：美國第61屆國際科技展覽會

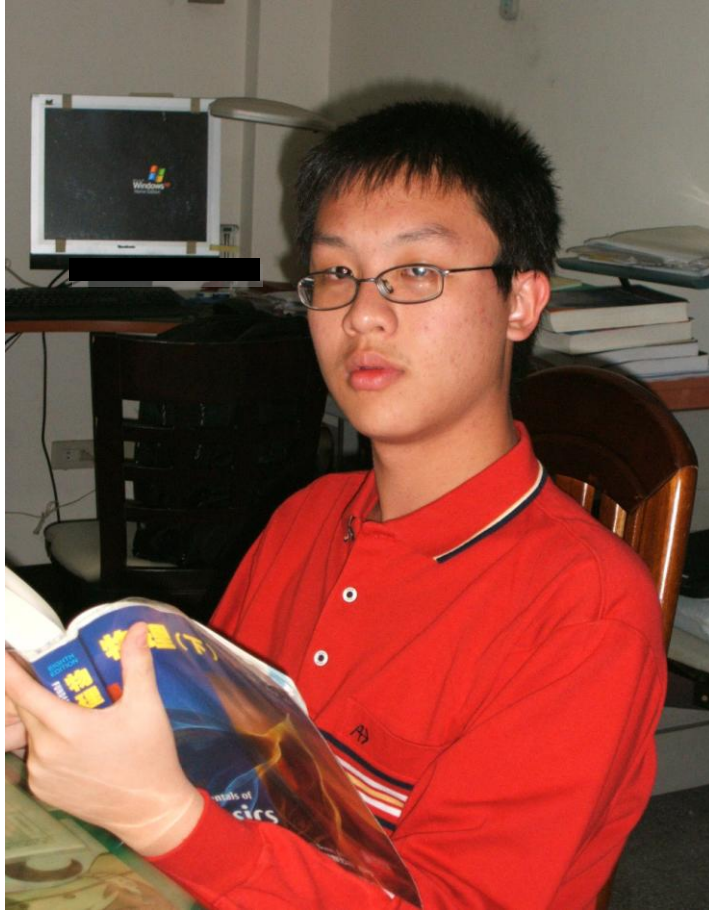
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關鍵詞：折射率梯度、擴散、擴散係數

## 作者簡介



我是黃宇晟，就讀於嘉義高中二年級。

我於國小階段就瘋狂的愛上科學，而其中物理是我的最愛，我現在參加清大高中科學資優學生培育計畫-物理組，學習物理的奧妙和獲得新知。我喜歡實驗，於國小即參與科展，雖然只在市賽拿到佳作，但這樣的成就激起我對科學的熱誠；於國中階段參加科展，順利進入全國賽並獲得第二名；這次由學長手中獲得這個科展的靈感，並在李文堂老師的帶領下，參加國際科展，希望能藉此機會把我的實驗與各位分享，並不斷學習相長。

## 摘要

溶液和水置於同一容器中，當溶液中的溶質向上擴散時，溶液的濃度會隨著高度改變，形成濃度梯度以及折射率梯度  $\frac{dn}{dy}$ 。

寬度  $a$  的透明方形盒，下方盛溶液，上方加入水，雷射光照射和鉛直成  $45^\circ$  的玻璃棒，再照射方形盒時，由於溶液的折射率梯度，雷射光在屏上形成鐘形曲線，向下偏  $Z$  的距離， $r$  為容器至屏的距離， $\frac{dn}{dy} = \frac{Z}{ar}$ 。

兩液原始交界處 ( $y=0$ ) 鐘形曲線最低位置 ( $Z$ ) 隨著時間 ( $t$ ) 改變，測量  $Z$  及  $t$  作  $\frac{1}{Z^2} - t$  圖，由其斜率可算出擴散係數  $D$ 。

濃度較高的二元混合液，例如甘油水溶液，當其重量百分率濃度未超過 70% 時，擴散係數仍不隨濃度改變；但在屏上所形成的鐘形曲線，其最大偏折點不但逐漸上升，還向甘油方偏移。測量偏移點所對應的液高 ( $y$ )，以及經歷時間 ( $t$ )； $y^2 = 2Dt$ ，作  $y - \sqrt{t}$  圖，由其斜率亦可算出甘油的擴散係數。

## Abstract

The mixing of a pure liquid and a solution in a vertical column produced a concentration gradient, which results in refractive index gradient  $dn/dy$ .

A He-Ne laser is directed onto a glass cylinder whose axis is perpendicular to the beam and  $45^\circ$  to the vertical, spreading the beam into a plane. The light striking a container of width  $a$  containing two liquids of two concentrations in contact produces a Gaussian curve on a screen at a distance  $r$  from the container owing to the refractive index gradient of the solution. The maximum vertical deflection  $Z$  of the Gaussian curve varies with time  $t$ . By measuring the deflection at  $y=0$  of different time  $t$  and drawing the plot of  $\frac{1}{Z^2} - t$ , we can get the diffusion coefficient  $D$  of the solute.

As for diffusion between two binary mixtures such as water and glycerol, the diffusion coefficient was found to be sensibly independent of glycerol concentration up to about 70%. The maximum deflection  $Z$  of the Gaussian curve not only shortens with time but also tilts to the glycerol side. We measure the tilting distance related to the height of liquid  $y$  and time  $t$ . We can get the value of  $D$  from the plot of  $y - \sqrt{t}$ . Values of the diffusion coefficient measured by the two simple methods have the same result.

We have presented a simple experimental technique whereby one may determine the diffusion coefficient of solute particles in a liquid. The results are in reasonable agreement with those obtained from more sophisticated techniques

## 一、研究動機：

學長以「利用雷射光的偏折測量擴散係數」測量低濃度水溶液溶質的擴散係數，參加全國第 49 屆科展獲獎；經驗傳承時，作者想到一個簡易的方法可以測量高濃度水溶液溶質的擴散係數。

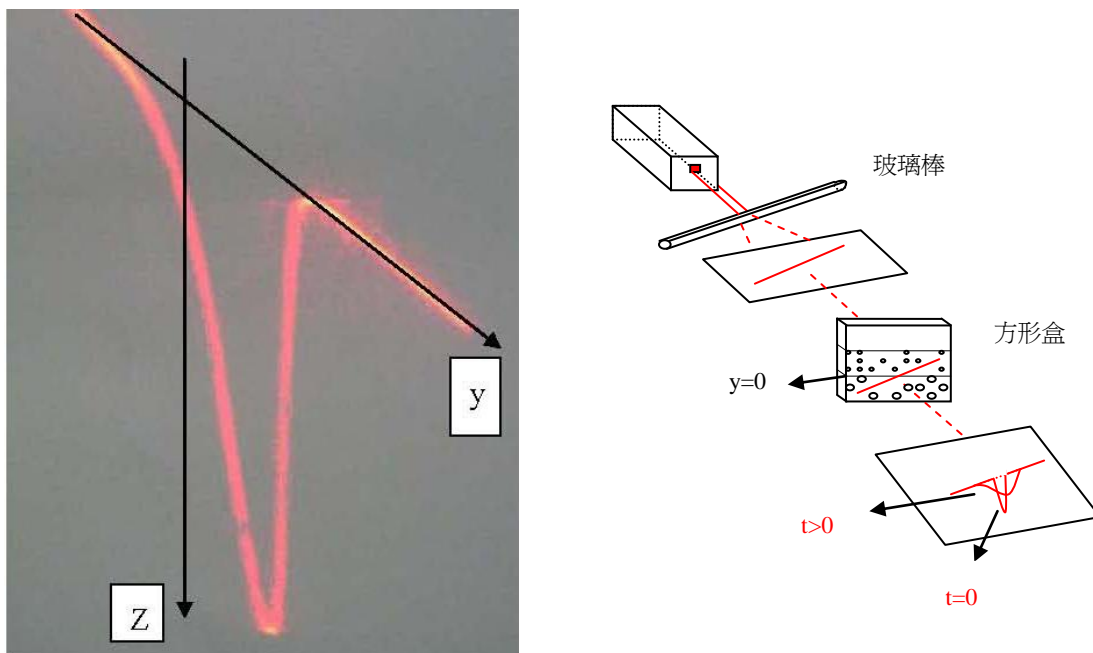
## 二、研究目的：

1. 利用雷射光照射兩液原始交界處，測量溶質的擴散係數。
2. 利用高濃度水溶液最大偏折點和時間的關係測量溶質的擴散係數。

## 三、研究背景：

1. 水溶液中溶質的擴散係數甚小(CGS 制中數量級為 $10^{-6} \sim 10^{-5}$ )，所用到的公式為指數函數，而且待測變因高達 7 個 [詳見公式(4)]，所以很難準確的測量。
2. 第 42 屆全國科展高中物理科得獎作品：「利用雷射光的偏折研究溶液的折射率梯度」，雷射光照射和鉛直成 $45^\circ$ 的玻璃棒後，照射下層盛硫代硫酸鈉水溶液，上層盛水的方形盒，在屏上出現鐘形曲線，由曲線的分佈作折射率梯度( $\frac{dn}{dy}$ )對高度(y)的關係圖，沒有測出擴散係數。
3. G. Gaffney(2001)利用雷射光照射硫代硫酸鈉水溶液，作出 $\frac{dn}{dy} - y$ 圖，再由文獻資料上查得硫代硫酸鈉的擴散係數(D)，代入高斯曲線公式畫出高斯曲線，和實驗結果的 $\frac{dn}{dy} - y$ 圖比較。G. Gaffney 等人也沒有真的測量擴散係數。
4. 第 49 屆全國科展高中物理科得獎作品：「利用雷射光的偏折測量擴散係數」學長將指數函數化成線性函數，可算出低濃度水溶液溶質的擴散係數。
5. 作者設計一個更簡易的方法，只要測量兩個待測量，即可算出高濃度水溶液溶質的擴散係數。

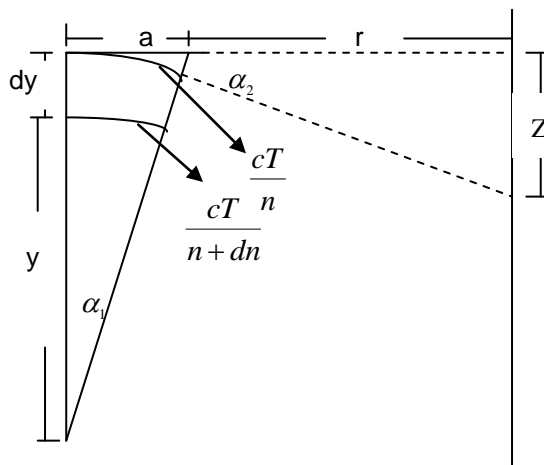
#### 四、原理：



圖一：雷射光經玻璃棒折射成一條和鉛垂線夾角  $45^\circ$  的斜直線，經過待測液後，因為溶液的折射率隨高度改變，所以在屏上呈現鐘形曲線， $y$  為方形盒中液體高度， $Z$  為鐘形曲線的最低位置。

1. 方形盒寬度  $a$ ，盛有液體，溶質的濃度由下向上漸減時，折射率亦漸減，距底部  $y$  及  $y+dy$  處，折射率分別為  $n+dn$  及  $n$ 。

圖二所示



圖二：雷射光在溶液中的偏折。

$$\alpha_1 = \frac{ct/n + dn}{y} = \frac{ct/n}{y + dy} \Rightarrow \frac{dn}{dy} = \frac{n}{y} = \frac{Z}{ar} \dots (1)$$

c：真空中的光速，t：時間。

$$2. (1) \text{Fick 第一定律得 } J = -D \frac{\partial C}{\partial y},$$

J：單位時間通過某截面的粒子數，

D：擴散係數，C：濃度。

$$(2) \text{Fick 第二定律 } \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}$$

(3) 方形容器下層盛待測液，上層裝水，令交界面處  $y=0$ ， $y < 0$  處  $C = C_0 =$  溶液的原始濃度； $y > 0$  處  $C=0$  只有水沒有溶質。

$$(4) \text{時間 } t \text{ 後，由 Fick 定律得 } C = \frac{C_0}{2} \left[ 1 - \text{erf} \left( \frac{y}{2\sqrt{Dt}} \right) \right] \dots (2)$$

當溶質的擴散係數不隨濃度改變時，將(2)式微分可得  $\frac{dC}{dy} = -\frac{C_0}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} \dots (3)$

(5) 當折射率和濃度成線性關係時，由  $\frac{dn}{dy} = \frac{dn}{dC} \cdot \frac{dC}{dy}$  可得

$$\frac{dn}{dy} = \frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} \dots (4)$$

$n_1$  為原始溶液的折射率， $n_2$  為水的折射率，此式為高斯函數，其軌跡稱為高斯曲線，又名鐘形曲線。

3. 在(4)式中， $y=0$  時  $\frac{dn}{dy} = \frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} \dots (5)$  量  $Z, a, r, n_1, n_2, t$  可得擴散係數 D。由(5)

式  $\frac{1}{Z^2} = \frac{4\pi D}{[(n_1 - n_2)ar]^2} t \dots (6)$  實驗時只要量 Z 及 t，作  $\frac{1}{Z^2} - t$  圖，斜率 =

$$\frac{4\pi D}{[(n_1 - n_2)ar]^2} \dots (7) \text{即可求出 D。}$$

4. 濃度較大的二元混合液，例如方形盒的下層加入濃度 70% 以下的甘油水溶液，上層加入水，甘油向上擴散時，雷射光照射形成的鐘型曲線，最大偏折點不但

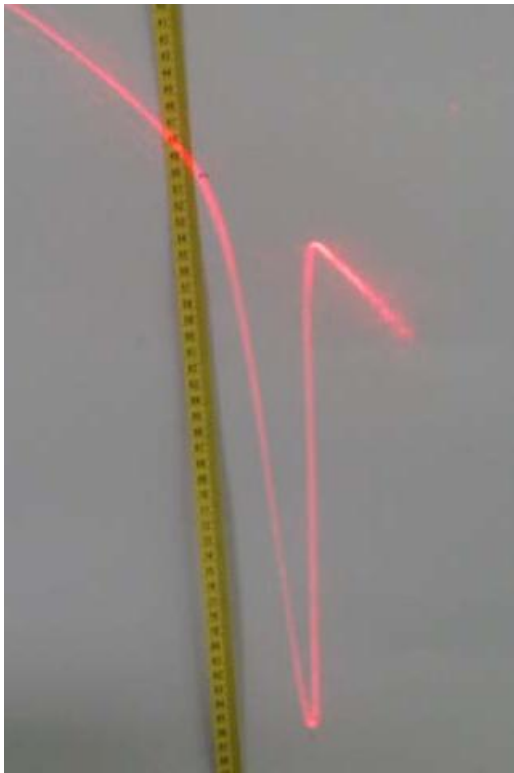
向上移，還向甘油方移動。圖三所示為 60% 的甘油水溶液擴散 300 分鐘，鐘形曲

線隨時間的變化。將公式(4)改為  $Z = \frac{ar(n_1 - n_2)}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}}$  ... (4) 取最大偏折位置 Z 對時

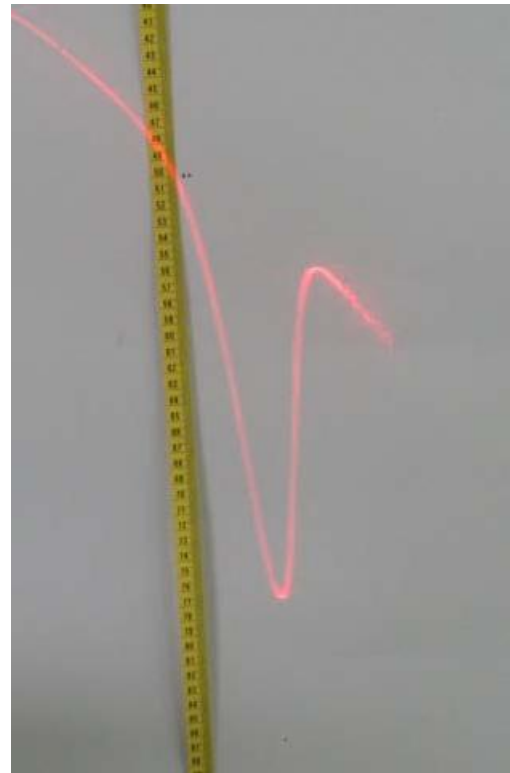
$$\text{間 } t \text{ 的偏微分 } \frac{\partial Z}{\partial t} = -\frac{(n_1 - n_2)ar\pi D}{4(\pi Dt)^{3/2}} e^{-\frac{y^2}{4Dt}} + \frac{(n_1 - n_2)ar}{2(\pi Dt)^{1/2}} \times \frac{y^2}{4Dt^2} e^{-\frac{y^2}{4Dt}}$$

$$\text{當 } \frac{\partial Z}{\partial t} = 0 \text{ 時，得到 } y^2 = 2Dt \dots (8)$$

換言之，測量鐘形曲線最低點所對應的方形盒的液高(y)，以及時間(t)，即可算出擴散係數。

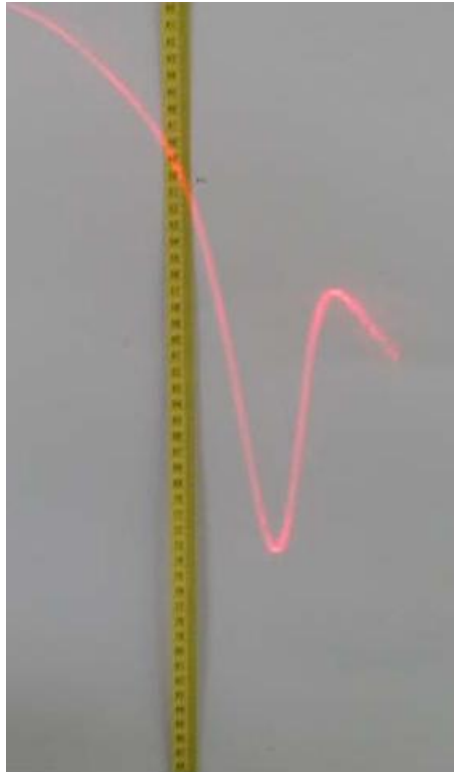


(a) 剛開始擴散。

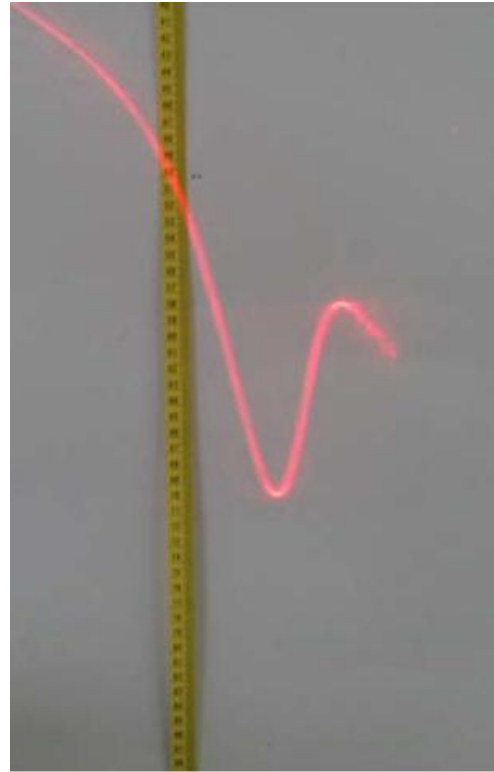


(b) 擴散 60 分鐘後。





(c) 擴散 150 分鐘後。



(d) 擴散 300 分鐘後。

圖三：方形盒下層放 60% 的甘油水溶液，上層放入水，鐘形曲線的最低點逐漸向右上(甘油)方偏。

## 五、器材：

1. 方形盒，壓克力製((10cm×10cm×1cm)
2. 玻璃棒(長 30cm，半徑 0.4cm)
3. He-Ne 雷射(2mW)
4. 紙屏、筆、硫代硫酸鈉、氯化銨、甘油等。

## 六、實驗步驟：

1. 測量水的折射率：雷射光照射貼有光柵的半圓形盒，測量繞射角  $\theta$ ，盒中放入水後，量得  $\theta'$ ，由  $\frac{\sin \theta}{\sin \theta'} = n$  量得水的折射率。
2. 測量溶液的折射率：和步驟 1 相同方法。
3. 方形盒下層放入 3 公分高的硫代硫酸鈉水溶液。用橡皮管將注射筒連接一針

頭，針頭緊貼著盒壁，緩注入水，需注意兩液的接觸面不要發生擾動，至水的高度亦為 3 公分。雷射光照射和鉛直成  $45^\circ$  的玻璃棒，再照射方形盒，在屏上貼一張白紙，屏上會出現鐘形曲線，每隔一段時間，用筆畫下曲線的軌跡。

4. 改換成不同濃度的甘油，重做上述實驗。
5. 測量方形盒寬度  $a$ ，盒到屏的距離  $r$ 。測量鐘形曲線相對應於  $y$  的下偏距離  $Z$ 。
6. 電腦作  $\frac{1}{Z^2} - t$  圖，求斜率以求  $D$  值。
7. 甘油水溶液放入方形盒內，高度 3cm，緩緩用注射筒加入 3cm 高的水。打開雷射，在屏上貼一張全開的白報紙，每隔 1 小時畫下鐘形曲線的最低點，以及  $y=0$  處所對應的  $Z$  位置。作  $\frac{1}{Z^2} - t$  圖，算出斜率，由公式 (7) 算出擴散係數。
8. 上步驟中，量取鐘形曲線最低點向右偏的距離，換算出對應的液高( $y$ )，作  $y - \sqrt{t}$  圖，算出斜率，由公式(8)，算出擴散係數。

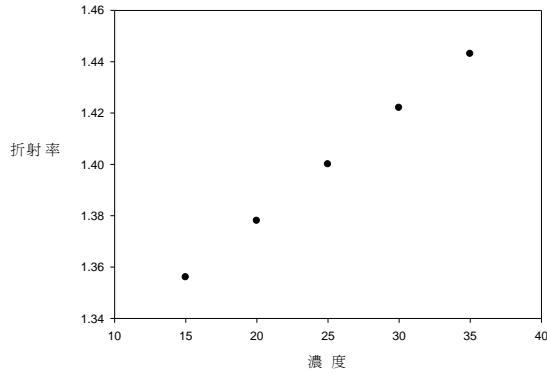
表一：硫代硫酸鈉水溶液的折射率隨濃度的變化( $25^\circ\text{C}$ )

	濃度	$\sin\theta$	$\sin\theta'$	N
1	15(%)	0.3955	0.2917	1.356
2	20(%)	0.3955	0.2870	1.378
3	25(%)	0.3955	0.2825	1.400
4	30(%)	0.3955	0.2781	1.422
5	35(%)	0.3955	0.2760	1.433

## 七、實驗結果：

1. 硫代硫酸鈉的水溶液的折射率隨濃度的變化如表一及圖四所示，所以(3)式

$$\frac{dC}{dy} = -\frac{C_0}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} \quad \text{可變為(4)式} \quad \frac{dn}{dy} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}}$$



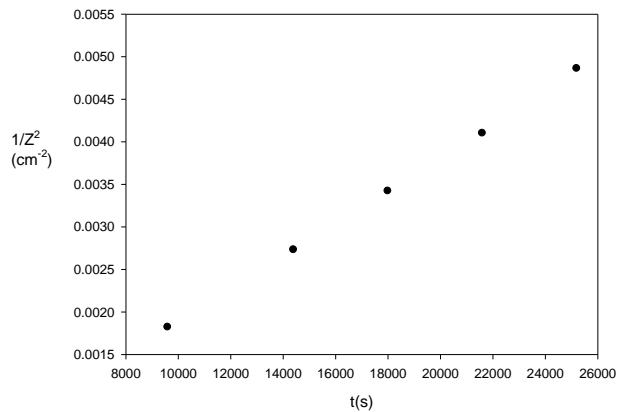
圖四：硫代硫酸鈉水溶液的折射率隨濃度(%)的變化。

2. 濃度 28% 的硫代硫酸鈉

的  $\frac{1}{Z^2} - t$  圖如圖五所示，其斜率為  $1.899 \times 10^{-7}$ ，又  $n_1 = 1.433$ ， $n_2 = 1.334$ ， $a = 1\text{cm}$ ，

$$r = 225\text{cm}，\text{由(7)式斜率} = \frac{4\pi D}{[(n_1 - n_2)ar]^2}$$

可求得  $D = 7.5 \times 10^{-6} \text{ cm}^2/\text{s}$ 。

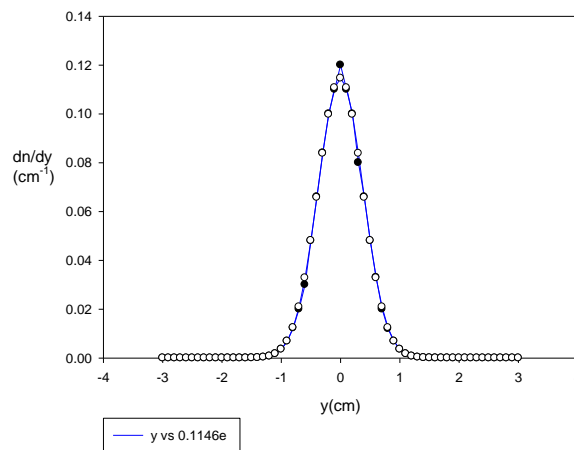


圖五：雷射光照射 28% 硫代硫酸鈉水溶液的偏折對時間關係。

3. 圖六的圓點為擴散 160 分鐘後的 28% 水溶液之  $\frac{dn}{dy}$  - y 圖為實驗結果，藍色的線為利用(4)

$$\frac{dn}{dy} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}}$$

$D = 7.5 \times 10^{-6} \text{ cm}^2/\text{s}$  作出的理論曲線。由圖可看出測量值和理論值十分吻合。



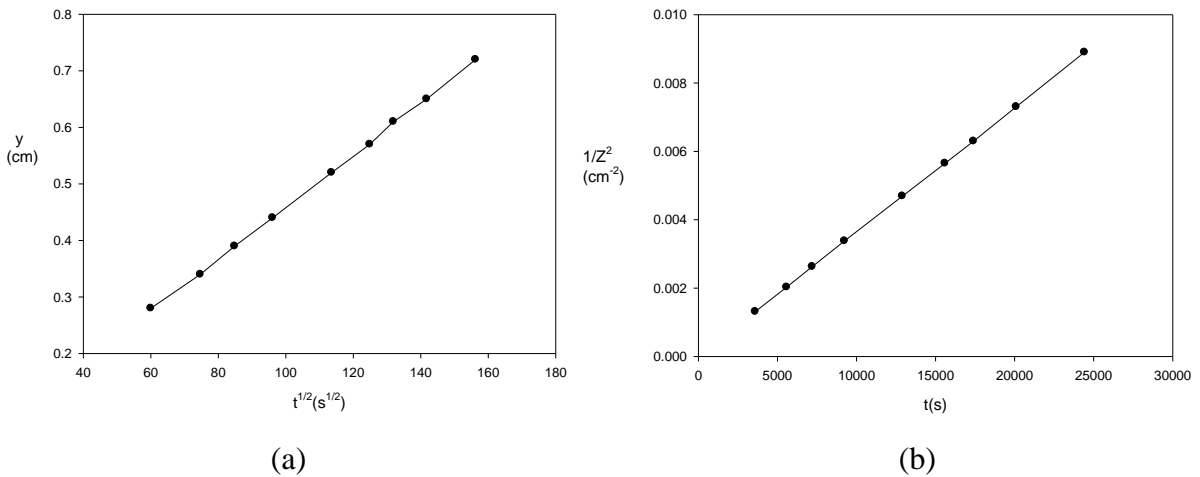
圖六：硫代硫酸鈉(28%)的  $dn/dy$  對  $y$  關係圖，藍色的線為理論值，圓點為實驗結果。

4. 用 60% 的甘油水溶液作實驗，實驗的結果鐘形曲線如圖三所示，曲線最低點所對應的液體在方形盒中的高度為(y)；Z 值為  $y=0$  處，鐘形曲線的位置，其數據如表二所示。

表二：60%的甘油水溶液曲線最低點所對應的液體在方形盒中的高度為(y)；Z 值為  $y=0$  處，鐘形曲線的位置

t(s)	y(cm)	Z(cm)
3600	0.28	27.6
5580	0.34	22.2
7200	0.39	19.5
9240	0.44	17.2
12900	0.52	14.6
15600	0.57	13.3
17400	0.61	12.6
20100	0.65	11.7
24420	0.72	10.6

5. 表二的數據作成圖七。



圖七：60%甘油水溶液的(a)  $y - \sqrt{t}$  關係圖。(b)  $\frac{1}{Z^2} - t$  關係圖

6. 圖七(a)的斜率為  $4.59 \times 10^{-3}$  由公式(8)  $y = \sqrt{2Dt}$  可求得擴散係數

$$D = 1.05 \times 10^{-5} \text{ cm}^2 / \text{s}。圖七(b)的斜率為  $3.63 \times 10^{-7}$  由公式(7)  $\frac{4\pi D}{[(n_1 - n_2)ar]^2}$ ，$$

60%的甘油水溶液的折射率=1.418，水的折射率=1.333，可求得擴散係數

$$D = 1.06 \times 10^{-5} \text{ cm}^2 / \text{s}。和文獻資料所載十分吻合。$$

## 七、討論：

1. 本實驗測量液體的折射率  $n_1$ 、 $n_2$  為四位有效數字， $a$ 、 $r$ 、 $y$ 、 $Z$  至少二位有效數字， $t$  超過四位有效數字，算出來的擴散係數取二位有效數字。
2. 溶質的折射率為  $n_s$ ，溶劑的折射率為  $n_f$ ，濃度  $C$  的溶液的折射率為  $n$ 。

$$n^2 = n_f^2 + C(n_s^2 - n_f^2) \dots (9), \quad \frac{dn}{dC} = \frac{n_s^2 - n_f^2}{2\sqrt{n_f^2 + C(n_s^2 - n_f^2)}} \dots (10)$$

但由實驗的結果如圖四顯示，濃度小於 28% 的硫代硫酸鈉水溶液，其折射率和

濃度的關係為線性。所以(3)式可以因  $\frac{dn}{dy} = \frac{dn}{dC} \cdot \frac{dC}{dy}$  改成(4)式。

3. 測量擴散係數要利用 Fick 第二定律  $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}$

數學處理後得 
$$C = \frac{C_0}{2} \left[ 1 - \operatorname{erf} \left( \frac{y}{2\sqrt{Dt}} \right) \right] \dots (2)$$

此式為誤差函數(error function)。

當溶質的擴散係數不隨濃度改變時，將(2) 式微分可得

$$\frac{dC}{dy} = -\frac{C_0}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} \dots (3)$$

當折射率和濃度成線性關係時，由  $\frac{dn}{dy} = \frac{dn}{dC} \cdot \frac{dC}{dy}$  可得  $\frac{dn}{dy} = \frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} \dots (4)$

利用公式(4)求擴散係數時，必須測量  $n_1$ 、 $n_2$ 、 $a$ 、 $r$ 、 $y$ 、 $Z$  和  $t$  等 7 個物理量，

而且該公式為指數函數，測量的結果代入公式後，經誤差傳遞後得到的  $D$  值

很容易形成甚大的誤差。我們在實驗步驟 6 中，取  $y=0$ ，使指數函數變

成  $\frac{dn}{dy} = \frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} \dots (5)$ ，得到  $\frac{1}{Z^2} - t$  關係為線性函數，而且只有先量取  $Z$

和  $t$  兩個物理量，求出斜率後，再代入測到的  $a$ 、 $r$ 、 $n_1$  和  $n_2$  即可得擴散係數  $D$ ，

方法簡單，準確度又高。

4. 硫代硫酸鈉的擴散係數不隨水溶液的濃度改變；由圖五可看出  $\frac{1}{Z^2}$  對時間  $t$  的

關係為線性，所以可利用本實驗測量擴散係數。而且由圖六可看出將測得的擴

散係數代入(8)式得到  $\frac{dn}{dy} - y$  的理論高斯曲線，和實際實驗的  $\frac{dn}{dy} - y$  圖十分吻

合。

5. 在實驗步驟 7 中，只測量  $y$  和  $t$  兩個物理量，作  $y - \sqrt{t}$  圖，算出斜率，由公式(8)，

即可算出擴散係數，方形盒內的液高雖只 3cm，但雷射光經玻璃棒折射擴大後，

照射方形盒，在屏上的投影超過 30cm，所以也可以很準確的換算出  $y$  值。本方

法適合測量濃度較高的液體，因為液體濃度太小時，右偏的  $y$  值太小，不易準

確的測量。

6. 從文獻資料知測量擴散係數有：雷射光偏折法、Moiré pattern法、干涉條紋法等十餘種，1975年Barnard所發展出來的雷射光偏折法被公認為最好的方法，本實驗採用此方法，且將數學式簡化，可以方便又準確的測量擴散係數。

## 八、結論：

本實驗利用很簡單的器材以及光的折射、繞射現象可以測量液體的折射率及折射率梯度，並算出擴散係數。測量擴散係數需要用到相當複雜的工程數學，本實驗針對擴散係數不隨濃度改變的物質，將數學式簡單化，可以測量出擴散係數，所得的結果和  $\frac{dn}{dy} - y$  圖以及文獻資料所載十分吻合。

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**Nonlinear diffusion dynamics measured by using  
a simple light transmission method**

*2010 ISEF Taiwan Finalist Physics*

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Project ID : PH015



## **Introduction**

Refractive index of a liquid depends strongly on the concentration of the solution. It is known that a concentration gradient will be generated in the interface regime when two different liquids are brought in contact. When a line laser beam is directed onto the interface of the two different liquids, it will produce a Gaussian profile upon transmission [1]. The transmitted Gaussian profile is very sensitive to the concentration gradient in the interface regime [2]. We set up a simple apparatus which is able to measure this transmitted profile at various time. By measuring the time evolution of such transmitted Gaussian profiles [3], the diffusion dynamics between two different liquids can then be revealed.

## Motivation

The first time I came across diffusion dynamics was when I was learning chemical kinetics. Figuring out the diffusion mechanism can help me to understand the rate constant. Being curious about this subject, I asked my teachers for more information about it. They then suggested that I should read journals like American Journal of Physics to get more information about diffusion mechanism and its related diffusion coefficient. However, the way nowadays scientist use to measure diffusion coefficient frustrated me due to its complicated mathematics. Also, what will be revealed from the measured diffusion coefficient with the other physical parameters also interests me. Thus I design a series of experiments, hoping to find out a better and easier way to measure diffusion coefficient and the factors that may impact it.

## Research Goals

1. Design simple and novel equipment to measure diffusion coefficient.
2. Study diffusion mechanism.
3. Take glycerol and sodium thiosulfate as an example to study the factors like temperature and concentration which may affect the diffusion.
4. Studying time evolution of diffusion for certain concentration and temperature.
5. Figure out the diffusion mechanism in water/glycerol-water solution and sodium thiosulfate-water solution.

## Apparatus

1. A container
2. A glass rod
3. He-Ne laser
4. Water bath
5. Samples : glycerol, sodium thiosulfate

(a)



(b)

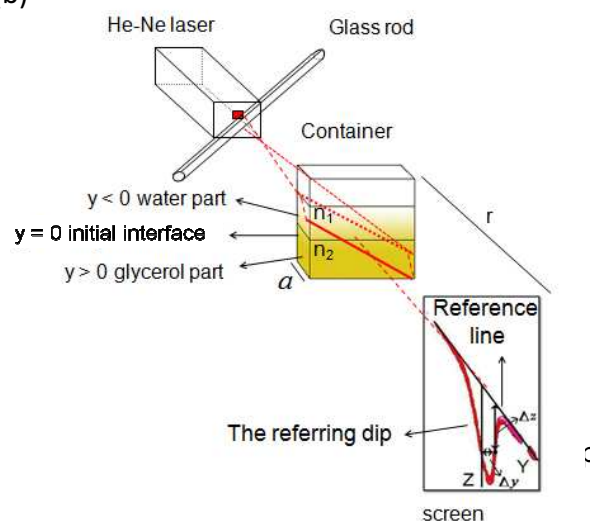


Fig. 2 (a) Photo and (b) Schematic illustration of the experimental setup

## Background Knowledge

Fick's first law:  $J = -D \frac{\partial C}{\partial y} - (1),$

Fick's second law:  $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} - (2),$

1. A container with width  $a$  is filled in the diffusing liquid. When the refraction index reduces from the top of the container as shown in Fig 3,

we have:  $\alpha_1 = \frac{ct/n + dn}{y} = \frac{ct/n}{y + dy} - (3) \Rightarrow \frac{dn}{dy} = \frac{n}{y} = \frac{Z}{ar} - (4),$

2. At  $t = 0$ , let  $y = 0$  for the interface of the liquid;  $y > 0$  for glycerol part;  $y < 0$  for water part.

3. For  $t$  is greater than 0, I get  $C = \frac{C_0}{2} \left[ 1 - \operatorname{erf} \left( \frac{y}{2\sqrt{Dt}} \right) \right]$

and  $\frac{dC}{dy} = -\frac{C_0}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} - (5)$  from Fick's law.

4. From chain rule  $\frac{dn}{dy} = \frac{dn}{dC} \cdot \frac{dC}{dy}$ , and combine Equation (4), (5), I get  $\frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}} - (6).$

When  $y = 0$ ,  $\frac{Z}{ar} = \frac{n_1 - n_2}{2\sqrt{\pi Dt}} - (7)$

5. Equation (6) can be rewritten as  $Z = \frac{ar(n_1 - n_2)}{2\sqrt{\pi Dt}} e^{-\frac{y^2}{4Dt}}$ , then  $\frac{\partial Z}{\partial t} = -\frac{(n_1 - n_2)ar\pi D}{4(\pi Dt)^{3/2}} e^{-\frac{y^2}{4Dt}} + \frac{(n_1 - n_2)ar}{2(\pi Dt)^{1/2}} \times \frac{y^2}{4Dt^2} e^{-\frac{y^2}{4Dt}}$

When  $\frac{\partial Z}{\partial t} = 0$ , I have  $y_{\max}^2 = 2Dt - (8).$

6. Stokes-Einstein equation :  $D = \frac{k_B T}{6\pi R \eta}$

Physical parameters:

$J$  : is the diffusion flux

$C$  : weight concentration

$n$  : refractive index of the liquid

$D$  : diffusion coefficient

$t$  : duration time

$T$  : temperature of diffusion

$a$  : width of the container

$r$  : distance between the screen and container

$y$  : position relative to the initial interface

$z$  : vertical shift of the dip

$y_{\max}$  : the  $y$  position at  $z$  maximum

$\eta$  : viscosity of solution

$R$ : the radius of the solution particle

$K_B$ : Boltzmann's constant

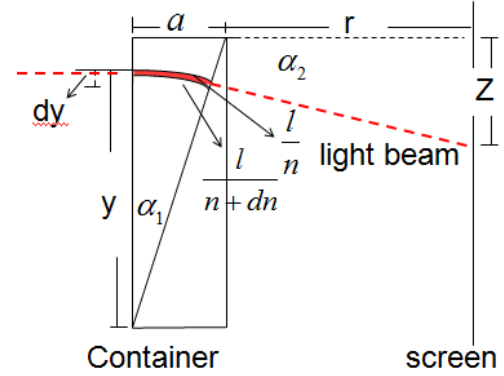


Fig. 3 schematic illustration of the tilt of laser beam as it pass through a solution with refraction gradient

## Methods and Experimental Procedures

1. The solution with temperature T is poured into the container up to 3 cm height, and then fill the container with water very slowly up to 6 cm height.
2. A glass rod tilted 45° to the vertical line. Direct a laser beam through this rod to strike the container. Then the transmitted laser beam is projected on a screen
3. Measure the displacement on the y and z axis on the time evolution transmitted profile, the following methods are applied to measure the time evolution diffusion coefficient, thus reveals the diffusion dynamics.
4. From the transmitted curve, there are two methods to get the diffusion coefficient D :

A. The method to apply equation (7) :

- (1) This method leaves out the exponential function. It can be applied in the liquid that has no significant variation in the y axis, such as sodium thiosulfate-water solution.
- (2) To calculate the error associated with each estimation of the diffusion coefficient D, in equation (7)  $\Rightarrow D = \frac{[ar(n_1 - n_2)]^2}{4\pi Z^2 t}$ . Standard rules for propagation of errors are then applied.

If we denote the error associated with D by  $\Delta D$ , then  $\Delta D = -\frac{2[ar(n_1 - n_2)]^2 \Delta Z}{4\pi Z^3 t} = -\frac{2\Delta Z}{Z} D$ ,

where  $\Delta y = \pm 0.02 \text{ cm}$ . The error  $\Delta D$  is about 0.4~0.07D.

B. The method to apply equation (8) :

- (1) This way not only leaves out the exponential function, also just two parameters have to be put in. This not only makes calculate much easier, but also increases the accuracy.
- (2) To calculate the error associated with each estimate of the diffusion coefficient D, in equation (8)  $\Rightarrow D = \frac{y^2}{2t}$ . Standard rules for propagation of errors are then applied. The

error associated with D by  $\Delta D$ , then  $\Delta D = \frac{y\Delta y}{t} = \frac{2\Delta y}{y} D$ , where  $\Delta y = \pm 0.02 \text{ cm}$ . The error

$\Delta D$  is about 0.4~0.1D.

## Results and Discussion

1. Sodium thiosulfate-water solution at 20°C weight concentration 21%, the variation of  $1/z^2$  with time is shown as figure 4. The diffusion coefficient calculated by method A is

$7.5 \times 10^{-6} \text{ cm}^2/\text{s}$ . These results correspond to

the theoretical value [5]. Because there is no significant variation in z axis, I will not apply the method B to get D.

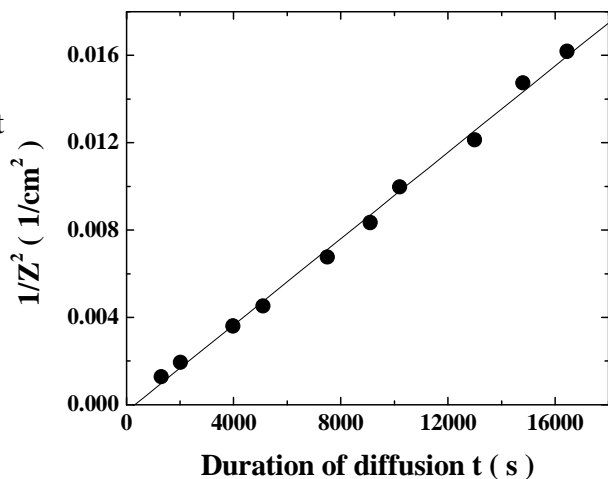


Fig. 4 The variation of  $1/z^2$  with time

2. Water/glycerol-water solution at 20°C weight concentration 60%. The variation of  $1/z^2$  with time, and  $y$  with time at the power of half is shown as figure 5. The diffusion coefficient calculated by method A is  $1.46 \times 10^{-5} \text{ cm}^2 / \text{s}$ ; calculated by method B is  $1.07 \times 10^{-5} \text{ cm}^2 / \text{s}$ , these results is quite near the theoretical value.[5]

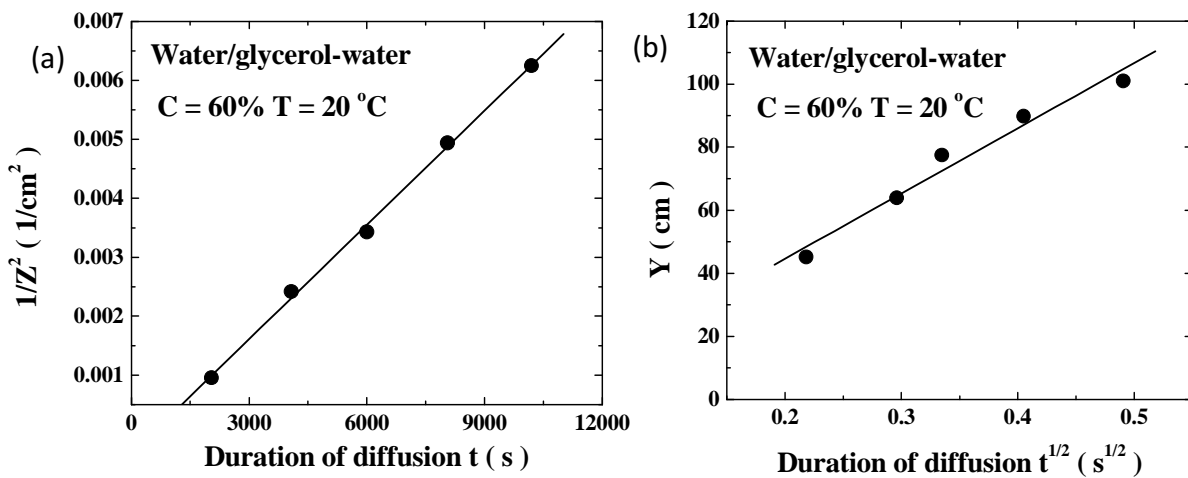


Fig. 5 The variation of (a)  $1/z^2$  with Duration time, (b)  $y$  with  $t^{1/2}$

3. The asymmetric profile of the  $dy/dn$  curve observed for the water/glycerol-water solution (Fig. 6, filled squares) shows that the diffusion in such a system occurs in both directions, where water and glycerol molecules can effectively diffuse into each other.
4. The symmetric profile of the  $dy/dn$  curve observed for the water/sodium thiosulfate-water solution (Fig. 6, filled circles) reflects that the diffusion occurs only around the interface regime.

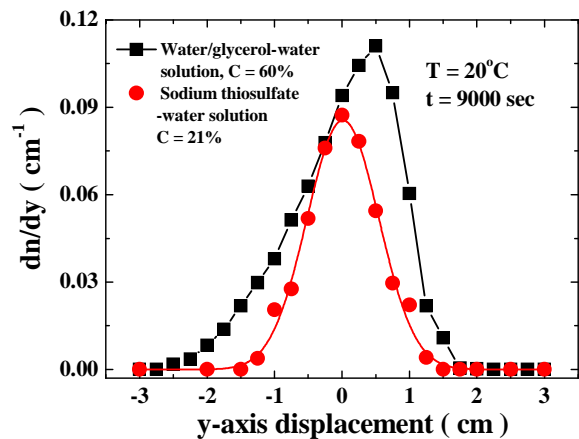


Fig. 6 Comparison of  $dy/dn$  along the y-axis direction for water to diffuse into the two solutions.

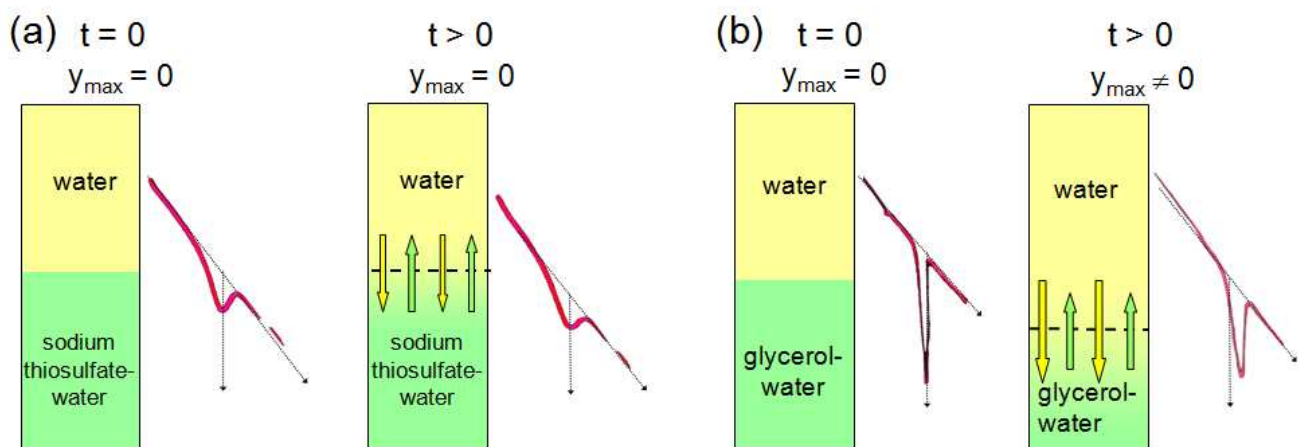


Fig. 7 Schematic illustrations of diffusion dynamics of (a) Sodium thiosulfate-water solution. (b) Water/glycerol-water solution, where  $y_{\text{max}}$  indicates the position of the maximum of  $dn/dy$  along y-axis.

- The thermal diffusion coefficient of the glycerol-water solution exhibits a sharp increase above 303 K (Fig 7), which can be described using an exponential increasing function (solid line).
- The sharp change can be originated from the breaking of glycerol-glycerol bond, which allows the formation of hydrogen bonds between water and glycerol molecules to form water-glycerol complexes (Fig 9). The temperature constant  $T_0 = 303$  K obtained from the fit represents the temperature above which the thermal energy can effectively break the glycerol-glycerol complex to form water-glycerol complexes.

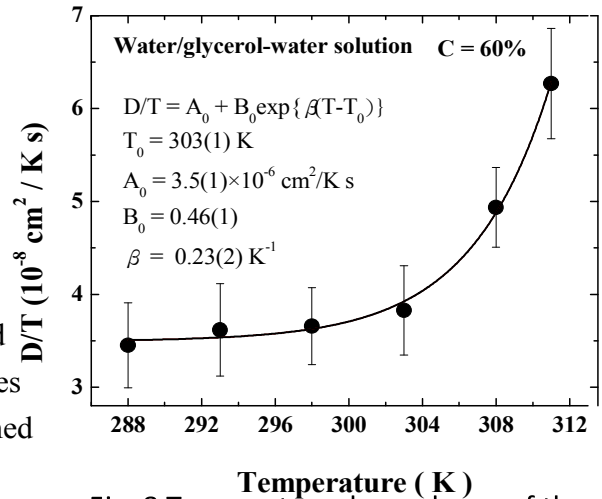


Fig. 8 Temperature dependence of the diffusion coefficient of water/glycerol-water solution.

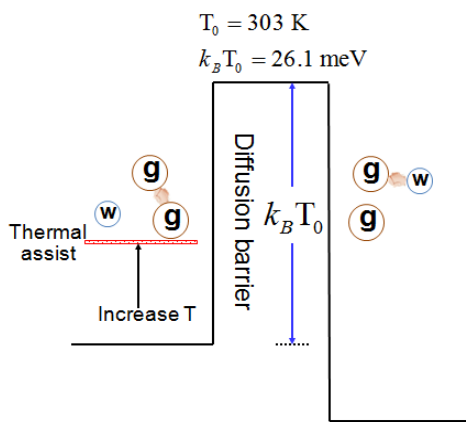


Fig. 9 Schematic illustration of the potential barrier for forming water-glycerol complex.

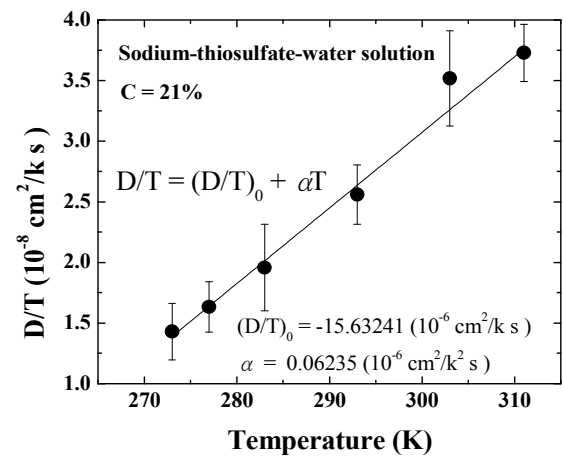


Fig. 10 Temperature dependence of the diffusion coefficient of sodium thiosulfate-water solution.

- The  $D/T$  of water/sodium thiosulfate-water solution increases linearly with increasing temperature, showing that there is no critical potential barrier for the diffusion at the room temperature regime. This character of  $D/T$  may reflect the diffusion to occur mainly in the interface regime.
- The higher diffusion coefficient for the solution with a higher glycerol concentration reflects that the interaction between glycerol and water molecules is noticeably stronger than that among glycerol molecules.

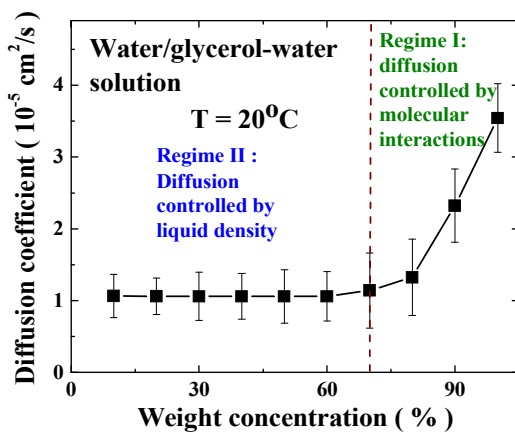


Fig. 11 Variations of diffusion coefficient of water/glycerol-water solution with duration of diffusion.

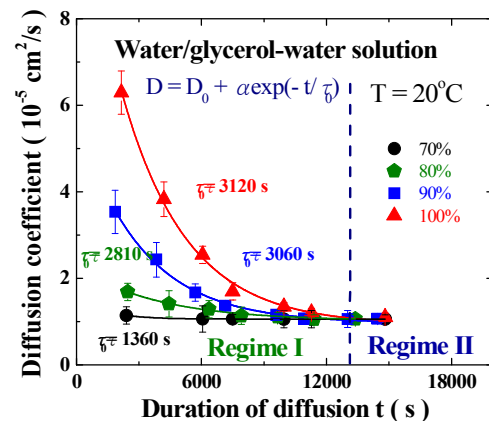


Fig. 12 Variations of diffusion coefficient of water/glycerol-water solution with weight concentration.

9. The diffusion coefficient of water/glycerol-water solution decays exponentially to a finite value within the duration of diffusion (Fig 8), showing that there are two mechanisms that control the diffusion. The diffusion coefficient exhibits a sharp increase when the glycerol weight concentration is higher than 70%, at which the molar ratio of glycerol/water is about 1/3 (Fig. 12).

10. If Stokes-Einstein equation <sup>[4]</sup> is valid, then product of D/T should depend on the viscosity. For sodium thiosulfate-water solution we can find out the T/D – η figure display a linear line, which imply that the Stokes-Einstein equation is valid. On other hand, in water/glycerol-water solution, it's not linear, thus it's cannot apply the Stokes-Einstein equation (Fig. 13). This may be caused by the intermolecular interaction between glycerol and water that triggers diffusion, making diffuse between glycerol and water not mainly determined by viscosity.

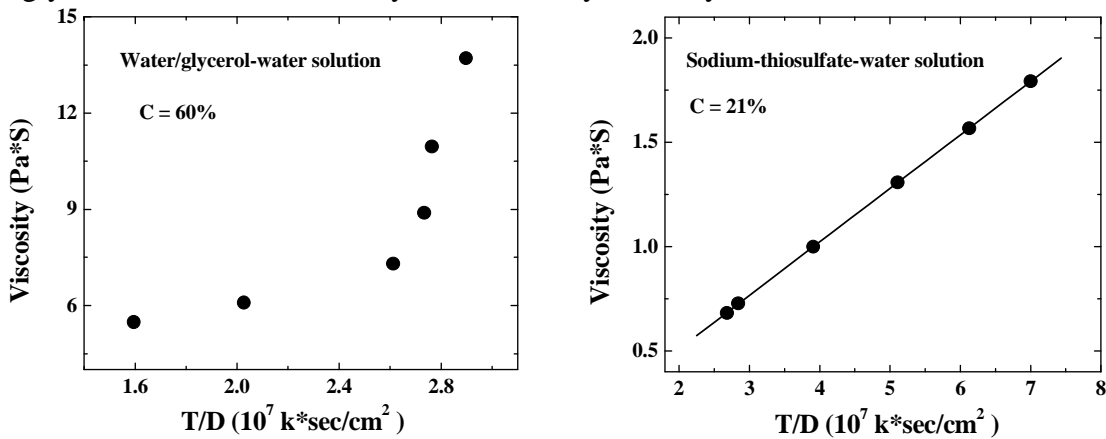
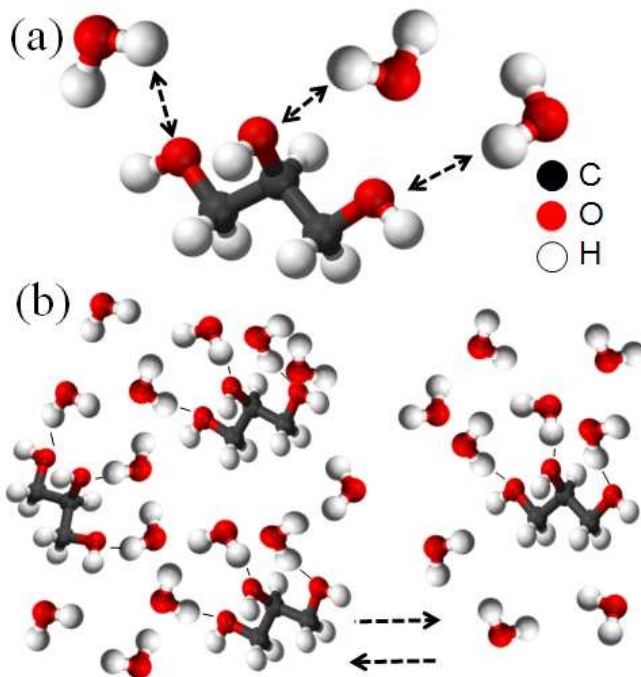


Fig. 13 Variations of viscosity with T/D of (a) sodium thiosulfate-water solution, and (b) Water/glycerol-water solution.

### The Mechanisms



There are three OH groups available for intermolecular bonding in each glycerol molecule.

1. Regime I : Diffusion controlled by inter-molecule interactions. In the present case, it is the formation of hydrogen bonds between glycerol and water molecules that trigger the diffusion (Fig. 14).
2. Regime II: Diffusion controlled by the similar but slight difference in water and glycerol densities

Fig. 14 Schematic illustration of the two mechanisms:

- (a) Regime I : C > 63%, intermolecular interactions, and  
 (b) Regime II : C < 63%, weight density diffusion.

## Conclusions

1. We provide a simple setup and an easy method to quantitatively determine the variation in diffusion coefficient during the process, which can qualitatively reveal the diffusion barrier. This method can also be used to measure other solutions.
2. A thermal energy higher than  $T_0=303$  K can effectively break the bonding between glycerol-glycerol molecules.
3. Two mechanisms that trigger the diffusion in water/glycerol-water solution have been identified. Inter-molecule interactions control the diffusion in high concentration, whereas the weight density differences between the liquids drive the diffusion when inter-molecule bonding have been saturated.

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