# Light extinction method for solubility measurement

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A novel measurement method for chemical solubility determination is brought forward, in which the advantages of two kinds of traditional methods are united. The results show that the concentration of unsolved particles suspending in the solution can be determined by measuring $I/I_0$ (ratio of the transmission intensity to the incident intensity) of the laser beam permeating through the solution according to Lamben-Beer law. The biggest relative deviation for the solubility data determined is less than 1.5% for the sparingly soluble substances and 0.3% for the opulently soluble substances. By comparison of the experimental solubility data with previous data, the light extinction method is demonstrated to be stable and reliable.

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Chemical solubility data are of great technical interest for their essential position in chemical engineering and chemistry researches. For long, solubility data are measured by using two kinds of traditional methods[1], namely, the isothermal method and the nonisothermal method. Generally, when the isothermal method is used, suitable analysis methods should be chosen as assistant approaches in order to get the accurate solubility data. However, for the sparingly soluble substances, it is often difficult to obtain the accurate solubility data by use of the isothermal method. Of course, the nonisothermal method may be effectual. For most of the nonisothermal methods, the dissolving process is observed and judged by the laser beam. The traditional laser method is called tangent method. The solubility is determined by judging the disappearing moment of the particles suspending in the solution. Because the dissolving speed and its driving force, $\Delta C$, are very low near the equilibrium point, the obtained solubility data are often lower than the real data. In this letter, a new experiment method for solubility determination, the light extinction method, is brought forward, in which the advantages of two kinds of traditional methods are united.

When a light beam transmits through the suspensions containing suspending particles, the transmitted light intensity is reduced because of the effect of scattering and absorption by the suspending particle. This phenomenon is called light extinction. According to Lamben-Beer law[2], the relationship between the incident intensity $I_0$ and the transmission intensity $I$ is

$$I = I_0 \exp(-\tau L), \tag{1}$$

where $I_0$ denotes the incident intensity (W/m$^2$), $I$ represents the transmission intensity (W/m$^2$), $\tau$ denotes the turbidity of the suspending particle (m$^{-1}$), $L$ presents the light traversing distance (m). For the simple situation, if there are $N$ spherical particles per unit volume whose diameters are $D$ in the solution, $\tau$ can be evaluated by

$$\tau = NK\sigma = \frac{\pi}{4} D^2 NK, \tag{2}$$

where $D$ denotes particle diameter (m), $\sigma$ represents the cross section (m$^2$), $K$ denotes the extinction efficiency factor, $N$ is the particle amount per unit volume (#/m$^3$).

For the common situation, the suspending particles are not of the same diameter, but with a certain particle size distribution. If there are $N_i$ particles with diameter $D_i$, the total turbidity $\tau$ is

$$\tau = \sum_{i=1}^{m} \frac{\pi}{4} D_i^2 N_i K. \tag{3}$$

By use of Mie-scattering law, Eq. (1) can be expressed as

$$\ln(\frac{I}{I_0}) = -\frac{\pi}{4} L \sum_{i}^{m} D_i^2 N_i K(\lambda, m, D_i). \tag{4}$$

The mass concentration of particles with diameters $D_i$ can be expressed as

$$w_i = \frac{\pi}{6} \rho D_i^3 N_i. \tag{5}$$

Then

$$\ln(\frac{I}{I_0}) = -\frac{3}{2} L \sum_{i}^{m} \left( w_i \frac{K(\lambda, m, D_i)}{\rho D_i} \right). \tag{6}$$

If the light beam is of multiple wavelengths, the relationship between $I$ and $I_0$ for each wavelength is

$$\ln(\frac{I}{I_0})_j = -\frac{3}{2} L \sum_{i=1}^{m} \left( w_i \frac{K(\lambda_j, m, D_i)}{\rho D_i} \right). \tag{7}$$

For solubility measurement, the laser beam may be regarded as one wavelength, so Eq. (7) may be written as

$$\ln(\frac{I}{I_0}) = -\frac{3}{2} L \sum_{i=1}^{m} \left( w_i \frac{K(\lambda, m, D_i)}{\rho D_i} \right), \tag{8}$$

$$\ln(\frac{I}{I_0}) = \sum \beta_i w_i L, \tag{9}$$

where $\beta_i$ is defined as light extinction efficient of particle $D_i$,

$$\beta_i = -\frac{3}{2} \frac{K(\lambda, m, D_i)}{D_i}, \quad i = 1, 2, 3, \cdots.$$

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By introducing the parameter, $\overline{\beta}$, which is the mean value of $\beta_i$, Eq. (9) can be written as

$$\ln(\frac{I}{I_0}) = \overline{\beta}wL. \tag{10}$$

At a lower concentration of suspending particles, Eq. (10) may be approximately expressed as

$$\frac{I}{I_0} = 1 + \overline{\beta}wL. \tag{11}$$

Thus, for lower concentration of suspending particles, the concentration of suspending particles may be calculated from Eq. (11) after the determination of $I/I_0$. Consequently, the solubility of corresponding substance may be determined by calculating the mass of dissolved particles. It is obvious that the advantages of two kinds of traditional methods were united.

The main apparatus used in the experiment are shown in Figs. 1 and 2. A semiconductor laser device with power of 5 mW emits a steady laser beam with wavelength of 650 nm. The laser beam traverses through the solubility measurement cell which containing a solution or slurry. If there is still solid in the path of the laser beam, the light will be scattered or absorbed and the transmitted intensity will be cut down. The more the solid existing in the solution, the less the light permeated. This trend can be seen in Fig. 3. The recorder takes down the intensity of the permeated light through the photovoltaic converter. 7-amino-cephalsporanic acid (7-ACA) was used as the experimental sample. The 7-ACA suspending solution was prepared by adding 500-ml deionized water and quantificational solid 7-ACA with precision of $\pm 0.0001$ g in the jacketed thermostat cell. By taking different volume suspending solution of 7-ACA into measuring cylinder (100 ml) in Fig. 2, the corresponding light intensity was taken down, as shown in Fig. 4. It shows the relationship between the intensity of the permeated light and the light travelling distance. The intensity of the permeated light was measured when the concentration of the suspending particle was changed. The relationship between $I/I_0$, $\ln(I/I_0)$ and the suspending particle concentration $w$ was shown in Fig. 5. From Fig. 4, it can be seen that $\ln(I/I_0)$ is linear with the light travelling distance by and large, so $\ln(I/I_0)$ and the light distance accord with Lamben-Beer law. But $I/I_0$ is greatly linear with the light distance with the relativity of $R^2 = 0.99$. From Fig. 5, it can be seen that the linearity between $I/I_0$ and the suspending particle

concentration is very well, so this linear relationship may be used for solubility measurement.

The solubility equilibrium cell is of approximately 600 cm$^3$. The magnetic stirrer works well enough to ensure the solute particles suspending in liquid phase. According to this measurement method, the weight of
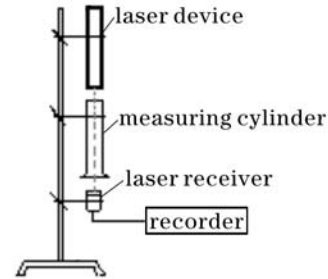


Fig. 2. Experimental setup for determining the relationship between the light intensity and light travelling distance.
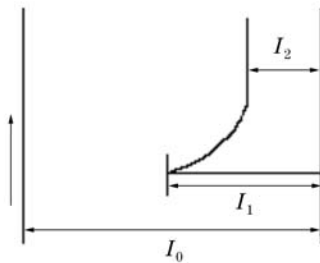


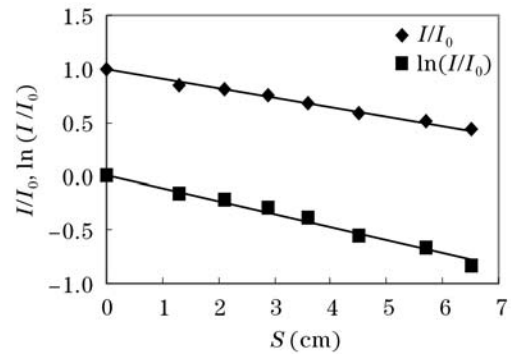Fig. 3. The sketch of the intensity of the permeated light changing with the particle dissolving.



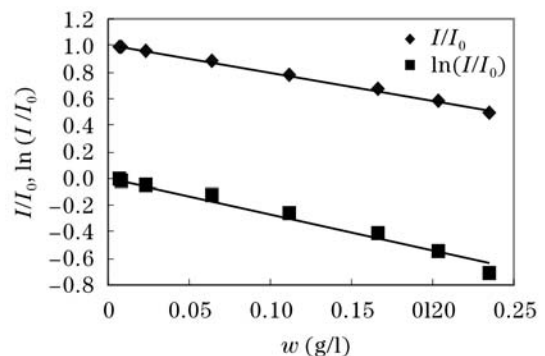Fig. 4. Relationship between the intensity of the permeated light and the light travelling distance $S$.



Fig. 5. Relationship between the intensity of the permeated light and the concentration of the suspending particles $w$.
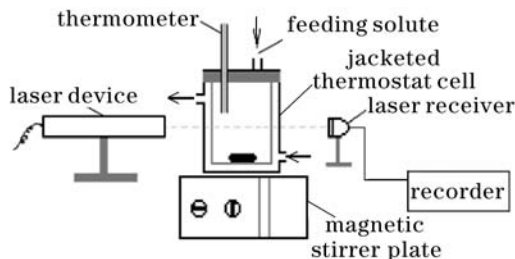


Fig. 1. Experimental setup for measurement of solubility data and determining the relation of light intensity and particle concentration.

**Table 1. Comparison of Our Experimental Solubility of Potassium Chloride in Water with the Literature Data**

| $t$ (°C) | | 10 | 20 | 25 | 30 | 40 | 60 |
|---|---|---|---|---|---|---|---|
| Light Extinction Method | Experimental Data (wt.-%) | 23.83 | 25.55 | 26.30 | 27.20 | 28.64 | 31.20 |
| | Relative Deviation (%) | 0.00 | 0.00 | −0.15 | 0.22 | 0.25 | −0.03 |
| Traditional Method | Experimental Data (wt.-%) | 22.90 | 24.72 | 25.66 | 26.71 | 27.72 | 30.34 |
| | Relative Deviation (%) | −3.90 | −3.25 | −2.58 | −1.58 | −2.98 | −2.79 |
| Data in Ref. [3] (wt.-%) | | 23.83 | 25.55 | 26.34 | 27.14 | 28.57 | 31.21 |

**Table 2. Comparison of Our Experimental Solubility of Silver Sulfate in Water with the Literature Data**

| $t$ (°C) | | 20 | 25 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|
| Light Extinction Method | Experimental Data (wt.-%) | 0.779 | 0.841 | 0.872 | 0.971 | 1.040 | 1.150 |
| | Relative Deviation (%) | −1.27 | 1.20 | −1.14 | 0.00 | −0.95 | 0.88 |
| Traditional Method | Experimental Data (wt.-%) | 0.738 | 0.770 | 0.838 | 0.916 | 1.012 | 1.068 |
| | Relative Deviation (%) | −6.56 | −7.21 | −4.76 | −5.61 | −3.58 | −6.35 |
| Data in Ref. [3] (wt.-%) | | 0.79 | 0.83 | 0.88 | 0.97 | 1.05 | 1.14 |

the solvent is fixed and added into the solubility equilibrium cell in advance. The key point is that while the solid solute is batch-type added into the cell, the mass of every batch is recorded. At the moment of the last batch of solute is added, the light intensity $I_1$ is noted down. With the solute being step-by-step dissolved, the light intensity will ceaselessly increase until the solubility equilibrium point. Here the light intensity $I_2$ is noted down. According to the value of $I_2/I_1$ and the mass of last batch solute added, the concentration of the suspending particles is calculated and the corresponding solubility can be gotten. For traditional laser method, at first the weight of the solvent and excessive solute are fixed, and the solvent is added into the solubility equilibrium cell till the beforehand added solute disappears. According to total solvent and solute amount, the corresponding solubility can be gotten.

It is noticeable that in order to make the measurement more efficient and get more accurate results, it is better to mill the solute initially.

To verify the reliability of this method, contrastive experiments were carried out with potassium chloride and silver sulfate. They are two representative substances, because the former is opulently soluble in water while the latter is sparingly soluble in water. The solubilities of these two substances in water were measured by the present method and traditional laser method, and the experimental data were compared with those published in Ref. [3] as shown in Tables 1 and 2. It is seen that the agreement between the experimental data by light extinction method and the literature data is very well. The reason is that the biggest relative deviation is less than 0.3%, average relative deviation is less than 0.05% for potassium chloride-water system, and the biggest relative deviation is less than 1.5% and average relative deviation is less than 0.22% for silver sulfate-water system. But for traditional laser method, the biggest relative deviation is less than 4.0%, average relative deviation is less than 3.0% for potassium chloride-water system, and the biggest relative deviation is less than −7.50% and average relative deviation is less than −6.0% for silver sulfate-water system, and the data determined by traditional laser method are all less than literature data. It shows that the traditional laser method has system deviation. That is to say, the presented method is more suitable and accurate for solubility measurement for all substances, from sparingly soluble solute to opulently soluble solute, than traditional laser method.

In conclusion, light extinction method presented in this letter is stable and reliable. It performs more objectively and brings little subjective error during measurements. The method meets simultaneously high and minor solubility determination's needs.

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