Science of light scattering of solvent undergoes evolution: improved spectrophotometric measurement rehabilitates Einstein-Smoluchowski equation

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ABSTRACT: The interests in determining the extinctions of solvents have largely revived due to their scientific implications and technological significance. Yet hitherto, the majority of spectrophotometric measurements over the visible spectral range has to involve the long-path length, usually over dozens of cm; the ultimate equation of computing the light scattering of solvents has not reached consensus. Here, we develop a simple, low-cost, and versatile methodology, attaining a sensitivity $10^{-4}$ dB/cm by only using 0.5 cm differential length, which makes a reduction of the path length by a factor of 100 while its closest approach to the record-low results. We rehabilitate Einstein-Smoluchowski equation to describe the light scattering of solvent, which has been a disfavor of use over the last 60 years. Our work further concludes that even the aforementioned equation cannot theoretically retrieve the scattering measured, prompting the need of an improved theoretical framework to reconcile the scattering peculiarity observed.

TOC GRAPHICS

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Extinction of chemically pure and optically transparent solvents generally results from absorption and scattering. Theoretical investigation and experimental quantification of the latter two physical properties of a solvent over a widespread wavelength range have attracted extensive and continuous interests over the last 100 years, in particular about H$_2$O. $^1$-$^{15}$ These research efforts are largely propelled by the human curiosity about how light interacts with solvent, as well as the essential role of these physical coefficients in many applications and research.

The absorption from ultraviolet (UV) to mid-infrared (MIR) wavelengths arises from the electronic transitions and vibrational resonances due to the molecular electronic and atomic polarizations. Approximated by the Morse Potential and resolved by the Schrödinger equation (or by the density functional theory), $^{15}$-$^{18}$ the energy frequencies and band strengths of those electronic transitions and vibrational resonances can be predicted to a good extent. In addition to the intrinsic absorption, light undergoes scattering upon its incidence on molecules. Thanks to the cornerstone work by many illustrious scientists, such as Rayleigh, $^1$ Smoluchowski, $^3$ Einstein, $^5$ Raman, $^4$ Debye, $^6$ Oppenheimer, $^9$ Kao, $^{19}$ etc., light scattering is accounted for by the theory of density fluctuation of a substance (i.e., mean square fluctuation of the dielectric constant). However, with regard to computing the light scattering of solvent, the ultimate formulation has not reached the consensus yet. $^8$, $^{13}$

From the practical perspective, the accurate measurement of extinction coefficient ($\mu$), absorption coefficient ($a$) and/or scattering coefficient ($b$) of solvent is equally compelling. On the one side, obtaining the exact numerical values of these coefficients represents a constant pursuit of human achievement in the record, which has been synchronized with state-of-the-art technological and methodological advancements. They include but not limited to preparing the highest-grade solvent and high-quality glass, as well as configuring the optical set-ups from conventional spectrophotometer to sophisticated approaches like adiabatic laser calorimetry, optoacoustic spectroscopy, and integrating cavity absorption meter. $^{11}$, $^{14}$ On the
other side, such coefficients are essential to fields as diverse as lidar bathymetry, detector construction for neutrino observation, imaging medium for multiphoton microscopy, photosynthetic process and biological primary production. The knowledge about the solvents’ coefficients is also of significance to evaluate the materiality of solvent, e.g., H$_2$O, used for industries (semiconductors, electronics, pharmaceuticals, etc.) as well as to capitalize optofluidics for applications from sensing, nonlinear optics to lasing. Yet, to acquire the exact extinctions of solvents in visible, e.g., H$_2$O, dozens or even hundreds of cm path length have been used over the last 100 years, in customized spectrophotometric setups; otherwise, large disagreements near the extinction minima are generated, as summarized in Table S1. For commercial practice, a widespread option is to use a 30 cm path length with an auxiliary integrating sphere to measure the extinction of H$_2$O. 

Optical paths of liquid-filled and empty cuvettes

One of goals of the present work is to develop a convenient, versatile and cost-effective methodology for a reliable spectrophotometric measurement, by only using the standard double-beam spectrophotometer. To this end, the complexity and difference of the optical paths that a ray of light undergoes in the liquid-filled and empty cuvettes are, at first, appreciated, as depicted in Section S2. Given that the thickness of the glass walls and path length of the cuvettes used are larger than 0.1 cm (and the spectral bandwidth > 2 nm), the light interference effect is neglected in this work.

As shown in the schematic diagrams in Figure S3, the total transmitted light $I_t$ contains the flux traversing the medium for once, thrice, and so on, during which it takes place with the multiple reflections and refractions at the interfaces of air-glass or glass-liquid, as well as the iterative transmissions through quartz glass and the medium. These reflections and transmissions, for an interface, are described by Fresnel equations

$$R_{tSiO_2} = \left(\frac{n_{SiO_2} - n_t}{n_{SiO_2} + n_t}\right)^2 \quad \text{and} \quad T_{tSiO_2} = 1 - R_{tSiO_2},$$

where $n_{SiO_2}$ and $n_t$ are the refractive indices of the cuvette and the medium (either air or filled liquid). The respective extinctions of quartz
glass and medium are given as \( T_{SiO_2} = 10^{-\mu_{SiO_2} L_{SiO_2}} \) and \( T_i = 10^{-\mu_i L_i} \) in accord with Beer-Lambert law (see Section S2.1).

For the liquid-filled cuvette, the numerical value of \( R_{SiO_2} \) at the interface of glass-liquid is negligible, e.g., at the scale of \( 10^{-3} \)-\( 10^{-5} \) for a pseudo solvent with refractive index from 1.3-1.5. As such, a fraction \( R_{air,SiO_2} \) of the incident light \( I_0 \) is reflected at the first interface, and the unreflected part is attenuated by a factor \( 10^{-\left(2\mu_{SiO_2} L_{SiO_2} + \mu_i L_i\right)} \) till the second air-glass interface. An amount of \( I_0(1 - R_{air,SiO_2})^2 10^{-\left(2\mu_{SiO_2} L_{SiO_2} + \mu_i L_i\right)} \) then exits as the first-order transmitted light; others at this interface are reflected and subjected to above process in iteration (Figure S3a). The whole process leads to an infinite series of different-order transmitted light (see Section S2.2), the total of which is summed as:

\[
I_{t,f} = I_0 \left(T_{air,SiO_2} T_{SiO_2}\right)^2 T_i (1 + \delta_f),
\]

where \( \delta_f \) is defined as the ratio of a total amount of the higher-order transmitted light to the first-order transmitted light, in the approximation to \( 0.001T_i^2 \). Since \( T_i \) of a medium varies with wavelength, \( \delta_f \) exhibits a spectral distribution.

The Eq. (1) suggests that \( T_i \) (or \( \mu_i \)) of a solvent can be extracted by using three strategies, as follows: (1) using the pre-determined numerical values of \( \left(T_{air,SiO_2} T_{SiO_2}\right)^2 (1 + \delta_f) \) in combination with the measured quantity of \( I_{t,f}/I_0 \); (2) using a sufficient long path length, so that, against the extinction of the filled liquid, the extinction contributions from \( T_{air,SiO_2} T_{SiO_2} \) are too small to be considered (i.e., the terms \( T_{air,SiO_2} T_{SiO_2} \) treated as unity); or (3) carrying out multiple measurements to completely compensate these cuvette-relevant terms, where, ideally, the measurements would use identical cells but with different optical paths. If the first method is even possible, attaining high-accuracy values of \( T_{air,SiO_2} \) and \( T_{SiO_2} \) of each face and wall of the cuvette is extremely laborious. Therefore, the latter two
strategies are usually adopted, for which the so-called One-step method and Two-step method have been developed (bottom and middle panels in Figure 1, respectively).

**Figure. 1** The flow chart describing the operations of Four-step measurement (top panel) versus the conventional approaches, including Two-step method (double-beam spectrophotometer, middle panel) and One-step method (single-beam spectrophotometer, bottom panel). The subscript annotations denote the path length ($L_{1,2}$) and the status of the cuvette ($e/f$ - empty or filled), and measurements in reference or sample compartment ($r/s$). For instance, with regard to the Four-step measurement, the incident and transmitted light, denoted as $I_0, I_{L1,e,s}$, $I_{L2,e,s}$, $I_{L3,e,f,s}$, $I_{L4,e,f,s}$, and $I_{L5,f,s}$ respectively, are depicted by arrows with the varied widths which indicate the attenuation of the radiant flux to different extents.

Though One-step method has delivered the record-low extinction coefficients $^{11}$, the requirement of using long path length makes the method expensive and (sometimes) complex, i.e., per shot, a large volume of solvents in provision to the amended spectrophotometers
(auxiliary apparatus added in commercial 23). This prompts us to look at the third strategy via a complete compensation of cuvette-relevant terms, for which measuring the empty cuvette (air as a medium) is also needed, in addition to the liquid-filled cuvette.

For the empty cuvette, as illustrated in Figure S3b, the first-order light traverses through four air-glass interfaces, at each of which a fraction of $R_{\text{air, SiO}_2}$ light is reflected. The latter undergoes multiple reflections and transmissions at the interfaces, yielding a series of higher-order light. The summation of different-order transmitted light leads to (full expression in Section S2.2):

$$I_{t,e} = I_0 \left( R_{\text{air, SiO}_2}^2 T_{\text{SiO}_2} \right)^2 T_{\text{air}} (1 + \delta_e),$$

where $\delta_e$ is approximately 0.007 (as the mean of 0.0063~0.0078 in the range of wavelengths concerned), analogy with a wavelength-independent item.

**Proposal of “Four-step measurement method”**

As shown in Table S1, the present compensation strategy, which is solely based on Two-step method, has not yet provided a satisfactory measurement on the extinction coefficient of solvent. As discussed in Section S3.3 (jointly with the concise description of the working principles of the spectrophotometer in Section S1.5), the evident deviation observed in Two-step method is largely ascribed to the inborn difficulties of completely cancelling out the cuvette-relevant terms. To overcome this issue, we propose to use “Four-step measurement method”, as schematically described in Figure 1 (top panel, detailed procedures in Section S3.1). In brief, by sequentially placing the cuvettes with different path lengths (only) in the sample compartment, e.g., 0.5 and 1.0 cm in this work, four individual spectrophotometric scans will be exercised to obtain the sets of absorbance of $A_{L1,e,s}$, $A_{L1,f,s}$, $A_{L2,e,s}$, and $A_{L2,f,s}$. 
In this manner, the extinction coefficient of a solvent can be calculated via (derivation given in Section S3.2):

\[
\mu = \frac{\Delta A_{L2,s} - \Delta A_{L1,s}}{L_2 - L_1} + \frac{Y}{L_2 - L_1},
\]  

(3)

where \(\Delta A_{L1,s} = A_{L1,f,s} - A_{L1,e,s}\), \(\Delta A_{L2,s} = A_{L2,f,s} - A_{L2,e,s}\) and \(Y\) is described as:

\[
Y = \log_{10} \left( \frac{1 + \delta_{L2,f,s} + \delta_{L1,e,s}}{1 + \delta_{L1,f,s} + \delta_{L2,e,s}} \right).
\]  

(4)

It must be noted that, only is the derivation of Eqs. (3) and (4) plausible when the cuvettes are identical, for which the terms relevant to cuvettes are cancelled out and \(Y\) is inconsiderable to be accounted (see discussions in Section S3.2). However, to stand out the decisive role and criteria of using cuvettes during spectrophotometric measurements, the omission of the trivia \(Y\) in Eq. (3) is avoided.

**Theoretical validation of “Four-step measurement method”**

The capacity of our methodology is theoretically evaluated by compiling the experimental uncertainties, including the systemic and random (measurement) errors. Note that the incident light is treated as the transverse electric (TE) mode, and the transverse magnetic (TM) light is not derived separately due to the high similarity.

The systematic errors are associated with the disturbance of the beams upon the detectors with the insertion of cuvettes in a spectrophotometer. The real light beams are not perfectly collimated, i.e., a paraxial ray. The insertion of the cuvettes makes an increase of the lateral displacement and diameter change of the light beams that traverse the cuvettes. These disturbances are escalated when the cuvettes are not completely flat and/or exhibit unparallel faces. Thus, the insertion of cuvettes will alter the beams which turn out be different from that used for the baseline correction. When accounted against the "zeroed" substance, such errors cannot be excluded from the measured absorbance.
The physical reasons underlying the systemic errors strongly suggest the Four-step method over the Two-step method. The dual beams of the spectrophotometer are highly similar but not identical. The concurrent use of a pair of cuvettes that are also highly similar but not identical prompts an increased extent of the alternations of the beams and thus their difference. As suggested in the discussion of Section S3.3, large deviations are, therefore, expected, which is in line with the observations in literatures (Table S1). In contrast, for the Four-step method, the beam passing through the reference channel is invariant (air is the fixed reference substance during the baseline correction and sample measurements) and only the adjacent beam in the sample compartment is subject to a distortion by the inserted cuvette. Such that, the bias imposed on the beams is minimized, by only perturbing one of two beams in the channels. This operational improvement seems a small step, but can effectively suppress the systemic errors, as evidenced by the experimental results as below.

The random (measurement) errors originate from that the light beams undergo the interface reflections and optical paths with varied extents, due in part to the non-identical cuvettes and in part to the off-normal incidence at an interface. The magnitude of the random errors depends on the variations of the (real) refractive index of the cuvette \(n_{SiO_2}\), the angle of incidence \(\theta\) at the interface) and the length of the cuvette \(L_i\). Given ignoring the inconsiderable \(Y\) in Eq. (3), a propagation of error of these variables yields the uncertainty of the extinction coefficient as (see the derivation in Section S4.1):

\[
S_\mu = \frac{1}{L - L_1} \sqrt{ \mu_2 S_L^2 + \frac{64}{(\ln 10)^2} \left( \frac{1}{n_{SiO_2}} - \frac{1}{n_{SiO_2} + 1} - \frac{1}{n_{SiO_2} + n_{i}} \right) ^2 S_n^2 }.
\] (5)

Eq. (5) suggests that the uncertainty of the measurement is primarily determined by the variables of the solvent measured and the cuvette used, but little depends on the change of \(\theta\). As shown in Figure 2a, for an angular incidence as large as 2.0° (the upper bound in practice), the relative errors of the absorbance imposed by \(\theta\) are capped under 0.185% and 0.055%, for
a pseudo solvent (refractive index at 1.3) with the extinction coefficient at 0.00001 and 0.1 cm\(^{-1}\), respectively; the relative errors are detuned to 0.172\% and 0.050\% with the increase of refractive index of solvent to 1.5.

**Figure. 2** (a) The relative error of the absorbance as a function of the angle of incidence (0-2°) for (pseudo) solvents with the extinction coefficients from 0.00001 and 0.1 cm\(^{-1}\) as well as with the refractive index of 1.3 and 1.5, respectively. (b) The dependence of the standard derivation (SD, left axis), \(S_\mu\), and the relative error from the SD (right axis), \(S_\mu/\mu\), on (pseudo) solvents with the extinction coefficients from 0.00001 to 0.1 cm\(^{-1}\) (the differential length 0.5 cm). As indicated by the vertical dash line, solvents usually exhibit the extinctions > 0.0001 cm\(^{-1}\), apart from H\(_2\)O and D\(_2\)O.

Eq. (5) is the analytic expression of \(S_\mu\) which lends us to readily obtain a numerical solution for the present experimental set up. For instance, the deviation of \(L_i\) is rationally at the same order as the thickness deviation of the cuvette which is specified by the manufacturer at ± 0.001 cm. The deviation of \(n_{SiO_2}\) of Suprasil® quartz glass for cuvette is approximated to ± 3×10\(^{-5}\).\(^3\) For the nominal differential path length 0.5 cm, \(S_\mu\) can be written as:

\[
S_\mu < 2\sqrt{0.00004 + 6\mu^2} \cdot 10^{-3}.
\] (6)

In accord with Eq. (6), \(S_\mu\) as a function of \(\mu\) is described in Figure 2b (dark yellow curve), which indicates that, for \(\mu\) smaller than 0.001 cm\(^{-1}\), \(S_\mu\) approximates 10\(^{-5}\) cm\(^{-1}\). By plotting
the relative error of the uncertainty \( S_\mu \) against the extinction of solvent \( \mu \) (Figure 2b, pink color curve), it is seen that, for the extinctions at 0.0001, 0.001 and 0.1 cm\(^{-1}\), our method gives rise to the relative error \( S_\mu / \mu \) about 12.6%, 1.3%, and 0.1%, respectively. These analyses attest that, by only using 0.5 cm differential length in the Four-step method, the extinction coefficients of solvents can be extracted reliably; by extending the differential length to 5 cm, our method can make the error < 3% for any solvents measured over a widespread wavelength range.

**Experimental validation of robust viability of Four-step measurement**

![Graph](image)

**Figure.** 3 The comparison of extinction coefficients of H\(_2\)O (a) and D\(_2\)O (b) measured in the wavelengths from 350-1400 nm. The grey and black lines stand for the experimental and smoothed data (via 50-60th percentile), respectively, obtained at room temperature (about 22 °C) in this work. The others are the broadly referred data from the publications as indicated. The observed leap of extinction of H\(_2\)O around 1380-1400 nm is ascribed to that the strong overtone of H\(_2\)O at 1470 nm (about 104 dB/cm) overshoots the instrumental detection capacity, which can be readily addressed by reducing the path length. For D\(_2\)O, the appeared spectral gap from 850-950 nm in the logarithmic expression was due to that the instrumental noise fluctuates the measured extinctions to trivial minus.

The viability of the Four-step measurement is experimentally proved by measuring the extinction coefficients of liquid H\(_2\)O and D\(_2\)O, two notable weakly-absorbing solvents. As shown in Figure 3, on comparing the results by Segelstein\(^{32}\) and by Sullivan\(^{33}\) (both widely
used as benchmark references), the mean % diff. of the minima of our work exhibit the decrease, about -22% for H₂O and -83% for D₂O, respectively (% diff. defined in Table S1). By consulting the extinctions coefficients broadly referred, the position and intensity of the extinction minima measured in this work show the most approximation to the record-low results given by Boivin et al., who, however, accomplished those by using a customized spectrophotometer with 50.3 cm path length (Boivin et al.: 0.000476 dB/cm at 405 nm for H₂O and 0.000478 dB/cm at 578 nm for D₂O, this work: 0.000656 dB/cm at 405 nm for H₂O and 0.0002495 dB/cm at 706 nm for D₂O). Compared to the report using the path length around 1 cm for H₂O, an improvement by a factor of 450 is observed in the present study. Referring to the recent study by Kedenburg et al. who employed a 4.0 cm cell for the extinction of D₂O, our work gives two orders of magnitude improvement but only using the fairly short differential path length – 0.5 cm.

The applicability and viability of Four-step method have been identified by the theoretical analysis and the experimental results, which attests the superiority of our method over the previous approaches, i.e., One-step and Two-step methods. As suggested by Eq. (6) and confirmed by Figure S4, the limit of Four-step method is determined by the instrumental own characteristics. To minimize the instrumental noises towards an improved spectrophotometric measurement, two spectrometers were used in a combination in this work (see Sections S1.4 and 1.5).

Extinction with molecular vibrations in dominance

For the wavelengths concerned, the electronic transition, light scattering and vibrational absorption conjointly constitute the extinction of solvent measured, but with varied extents in different spectral regions. For the sake of wavelength coverage, the spectral domain that almost exclusively involves overtones and combination bands of the vibrational quanta is investigated in the first place.
Figure. 4 Extinction coefficients of (a) H$_2$O and D$_2$O, as well as (b) DMSO and DMSO-d$_6$, expressed in the linear (top panels) and logarithmic (bottom panels) scales. The overtones and combination bands of the regular solvents are indexed by (pale blue) color-columns. Their deuterated counterparts with same quantum number exhibiting the red-shift vibrations are selectively indicated by (light magenta) color-columns. For H$_2$O and DMSO, the overtones concerned are lightly off the integer of the fundamental frequencies due to the anharmonicity. For D$_2$O, DMSO and DMSO-d$_6$, the spectral gap appeared in the logarithmic expression from 850-950 nm due to trivial minus values.
H$_2$O exhibits three fundamental vibrations associated with two OH bonds,\textsuperscript{35} including symmetric ($\omega_1$) and asymmetric ($\omega_3$) stretch, and bending ($\omega_2$), with resonances maxima of approximately 3277 cm$^{-1}$ (3.05 μm), 3490 cm$^{-1}$ (2.87 μm) and 1645 cm$^{-1}$ (6.08 μm), respectively. In addition to the weak rocking vibrations of CH$_3$ peaking at 1019 and 1031 cm$^{-1}$, DMSO bears with diverse pronounced resonances, such as the fundamental stretching vibrations from CH$_3$, CH$_2$, & CH bands in range of 2850-3000 cm$^{-1}$ (3.33-3.50 μm), the fundamental bending resonances from CH$_2$&CH$_3$-deformations between 1350-1470 cm$^{-1}$ (6.8-7.4 μm), the SO fundamental stretching modes from 1041-1052 cm$^{-1}$ (9.5-9.6 μm), and the CSC fundamental stretching vibrations from 667-697 cm$^{-1}$ (14.3-15.0 μm).\textsuperscript{16, 18, 36-37}

The overtones and combination bands of these fundamental vibrations form the characteristic absorptions of solvents in shorter wavelengths. As shown in Figure 4a, the absorption bands of H$_2$O at around 606, 739, 970, and 1200 nm are assigned as the $\nu$th harmonics of OH stretch modes as well as the combinations of the fundamental bending mode and stretch harmonics. As shown in Figure 4b, with regard to DMSO, the overtones of CH$_{1,2,3}$-stretching vibrations and CH$_2$&CH$_3$-deformations generate the absorptions with maxima at 627, 736, 901 and 1180 nm (2-9th overtones) and a span of 680-740, 756-822, 850-925, 971-1057, 1133-1233 and 1360-1400 nm (4-9th overtones), respectively. The overtones of CH$_2$&CH$_3$-deformations are only observable when they are not overlaid with CH$_{1,2,3}$-overtones; the overtones (or combination bands) of SO and CSC are undetectable over the wavelengths concerned.

For the deuterated counterparts, the elementary substitution of hydrogen by deuterium increases the reduced mass $m^*$, e.g., for diatomic bonds, $m^* = m_1m_2/(m_1 + m_2)$. As suggested by the relationship between the fundamental resonance frequency $\omega_0$, the reduced mass $m^*$ and force constant $k$ ($\omega_0 \sim \sqrt{k/m^*}$),\textsuperscript{38} the deuterium replacement detunes the vibrations and red-shifts the resonance wavelengths (indicated by arrows in bottom panels of Figure 4). For
instance, a red-shift of the fundamental resonances takes place for D$_2$O by a factor of about 0.728 ($m^*_{\text{OH}} \rightarrow m^*_{\text{CD}}$). In a similar fashion, the fundamental vibrations of DMSO-d$_6$ exhibit the red-shift by factors of about 0.735, 0.758, and 0.775 against the reduced mass changes of $m^*_{\text{CD}}/m^*_{\text{CH}}$, $m^*_{\text{CD}}/m^*_{\text{CH}_2}$ and $m^*_{\text{CD}}/m^*_{\text{CH}_3}$, respectively.

For a solvent, when the quantum number $\nu$ increases by one, the strength of overtones (and combination bands) is reduced by about one order of magnitude, $^{16,39}$ i.e., the intensity of higher-order harmonics in shorter wavelengths could be orders of less than that of the fundamental vibrations. This accounts for, in the wavelengths range concerned, (1) the drops of extinction intensities of H$_2$O and D$_2$O from fundamental vibrations till 5th harmonics, e.g., at 606 nm and 825 nm, respectively; (2) the undetectable harmonics of SO and CSC of DMSO as their low-lying fundamental vibrations are overcompensated herein; $^{16}$ (3) and the decrease of extinction intensities of CH-overtone of DMSO from fundamental vibrations to 4th harmonics, e.g., at 736 nm. However, as the wavelength continues to decrease, for H$_2$O and D$_2$O, the subsequent higher-order harmonics are unobservable; for DMSO, it seems that these higher-order harmonics become stronger relative to the prior harmonics, e.g., a ratio of about 0.43 between the strengths of 5th and 4th overtones observed. Indeed, the anomalies observed in the wavelengths of higher-order harmonics result from the superimposition of the progressively increased light scattering, the magnitude of which generally increases inversely proportional to the fourth power of wavelength. For different solvents, the transition wavelengths giving rise to the dominance of extinction from vibrational absorption to light scattering are varied. Figure 4 suggests that, for H$_2$O, D$_2$O, DMSO, and DMSO-d$_6$, these transition wavelengths are nearly at 570, 780, 736 and 1001 nm, respectively.

With regard to the pair of regular and deuterated solvents, for the vibrations with the same quantum number, Figure 4 shows a decrease of the magnitude of vibrations (e.g., the overtones and combination bands) of the deuterated solvents versus their protonated
counterparts, as evidenced by the ever-downward arrows in the figure. This is due to a smaller anharmonicity constant and a reduced fundamental band strength in the elementary substitution of hydrogen by deuterium. For the vibrations at the same wavelength, due to the additional red-shift of vibrational frequency, the strengths of the vibrational absorption of the deuterated substances shall undergo about one order of magnitude reduction compared to that by the protonated counterparts. As shown in Figure 4, this principle holds to the pair solvents of H$_2$O and D$_2$O almost till the wavelength of minima of D$_2$O; but in stark contrast, for DMSO and DMSO-d$_6$, at the wavelength of 5th CH overtone, the strength of extinction of DMSO only exhibits 1.5~2.0 times larger than that by DMSO-d$_6$. These observations are in agreement with the conclusion made in above paragraph that, as the wavelengths decreasing, the continuously decreased vibrations are met with and distorted by the progressively increased light scattering.

**Extinction with light scattering in role**

![Figure 5](image_url)

**Figure. 5** (a) The comparison of the scattering coefficients of H$_2$O from the experimental observations (derived) and the theoretical computations. The experimental absorption coefficients of H$_2$O were extracted from Mason *et al* 14, and its extinction coefficients are interpolated from the combined data of Segelstein 32, Boivin *et al.*, 11 and the present measurement. (b) The measured extinction coefficients of D$_2$O, DMSO, and DMSO-d$_6$ (depicted by solid lines, and the absorption coefficients not given due to their absence for these three solvents) overlaid with the computed scattering coefficients by Einstein’s equation (depicted by dash dot lines with the corresponding
colors). In computation, wavelength-independent $\beta_T$ and $\Delta$ (a weak function of wavelength over the visible range \(400\)) were taken from Table S2, and $n$ was from the paper on preparation by authors about the refractive index of solvents. Numerical values of \((\partial n / \partial P)_T\) of $H_2O$ were linearly extrapolated via the quantities by Kraotohvil et al. (from 365-546 nm) \(^9\).

To derive the scattering coefficient of a solvent (experimentally), the subtraction of the measured absorption coefficient from extinction coefficient is carried out, e.g., $H_2O$ from near 250 to 490 nm. As shown in Figure 5a, the absorption coefficient of $H_2O$ exhibits a dip with minima at 344 nm, \(^{14}\) representing a kink point of the respective tails of the first electronic transition and molecular harmonics. On comparing their quantities of the extinction, absorption and (derived) scattering coefficients, light scattering is seen to be leading for the extinction of $H_2O$ from 275-425 nm (weighing about $\geq$ 70% of the measured extinction). In fact, we speculate that the lower bound of the wavelengths where the scattering makes the major contribution to the extinction of $H_2O$ shall extend from 275 nm till UV cut-off wavelength of 190 nm \(^{41}\). Therefore, the comparison in Figure 5a implies the need for an improved measurement on absorption coefficients of $H_2O$. \(^{14}\)

To compute the scattering coefficient of solvent, three forms of equations, based upon the density fluctuation theory by Smoluchowski and Einstein, \(^5\), \(^9\) have been developed. Taking into account the depolarization ratio $\Delta$, the first equation given by Einstein in 1910 is expressed as:

$$\tilde{b} \, (\text{dB/cm}) = \frac{1}{10 \ln 10} \frac{8 \pi}{3} \frac{R_{tot} \, 2 + \Delta}{1 + \Delta}$$  \(\text{(7)}\)

$$R_{tot} = \frac{\pi^2}{2 \lambda_0^4} k T \beta_T \frac{(n^2 - 1)^2 (n^2 + 2)^2}{9} \frac{6 + 6 \Delta}{6 - 7 \Delta}$$  \(\text{(8)}\)

where $\tilde{b}$ is the scattering coefficient, $R_{tot}$ the Rayleigh ratio, a measure of the light-scattering power of a medium, $k$ the Boltzmann constant, $T$ the absolute temperature, $\lambda_0$ the wavelength.
of light in vacuum, $\beta_T$ the isothermal compressibility, $n$ the real part of refractive index at constant temperature (where “$T$” has been omitted for the sake of simplicity), and $(6 + 6\Delta)/(6 - 7\Delta)$ the Cabannes factor.

By re-expressing the density fluctuation at a microscopic level with the pressure derivative of the refractive index at constant temperature $(\partial n / \partial P)_T$ (so-called isothermal piezo-optic coefficient), Coumou et al and Kratohvil et al in 1960s re-formulated Eq. (8) as:

$$R_{tot} = \frac{2\pi^2}{\lambda_0^4} kTn^2 \frac{1}{\beta_T} \frac{\partial n}{\partial P}_T \frac{6 + 6\Delta}{6 - 7\Delta}$$

(9)

The proposal of Eq. (9) has made Einstein’s initial equation largely, if not completely, a disfavor of use over the last 60 years.

Though Eq. (9) is the most extensively used form to compute the light scattering of solvent hitherto, another revised equation was provided in 2009 by Zhang and Hu, which is written as:

$$R_{tot} = \frac{\pi^2}{2\lambda_0^4} kT \beta_T (n^2 - 1)^2 \left[1 + \frac{2}{3} (n^2 + 2) \left(\frac{n^2 - 1}{3n}\right)^2\right] \frac{6 + 6\Delta}{6 - 7\Delta}$$

(10)

The terms in either Einstein’s initial equation or Zhang & Hu’s formula are readily accessible, including the extensive database of $n$ and apparent measurement of $\beta_T$ (or deriving $\beta_T$ from more conveniently measurable surface tension $\gamma$ via equation of $\beta_T \gamma^{7/4} =$ constant). The values of $(\partial n / \partial P)_T$ in Eq. (9) are devoid of for the majority of solvents as well as difficult to be measured with high accuracy. Furthermore, given the (nearly) mathematical equality of $2 pn \left(\frac{\partial n}{\partial \rho}\right) = \frac{(n^2 - 1)(n^2 + 2)}{3} \approx \frac{2n}{\beta_T} \left(\frac{\partial n}{\partial P}\right)_T \approx (n^2 - 1)[1 + \frac{2}{3} (n^2 + 2) \left(\frac{n^2 - 1}{3n}\right)^2]$ ($\rho$, the density of solvent), we are strongly motivated to revisit Eqs. (8), (9) and (10). The earlier difficulty of obtaining the scattering coefficient exempt the (accurate)
absorption coefficient from the extinction coefficient also renders the previous justification deserved to be taken a second look.

As shown in Figure 5a, the comparison of experimentally derived and theoretically computed scattering coefficients demonstrates that Einstein-Smoluchowski initial equation gives the best approximation to the experimental quantities, from which the scattering strength is suggested to decline with a decrease of $\beta_T$ and $n$. By using the rehabilitated Einstein’s equation to compute the scattering coefficients of D$_2$O, DMSO, and DMSO-d$_6$, the scattering coefficients are predicted to be ranked as a sequence of H$_2$O < D$_2$O < DMSO-d$_6$ < DMSO, which agrees with the experimental observations (Figure 5).

However, Figure 5 also shows that, (1) for different solvents, the discrepancies of the computed scattering quantities (almost indistinguishable without zoom in) are much smaller than the apparent differences measured; and (2), for a solvent, the computed quantities of the scattering coefficient appear to be largely lower than that of its measured, particularly at the wavelengths with relatively small vibrational absorptions. As tabulated in Table S2, the yielded % diff. could be about 30% for H$_2$O, but showing upsurge for D$_2$O (900%), DMSO (3553%), and DMSO-d$_6$ (2250%). To exclude the large % diff. of the latter three solvents from the possible over comparison of the measured extinction versus the computed scattering, the same comparison is applied to H$_2$O and only a slight increase to 33% is obtained. This pertinent argument leads to the conclusion that the discrepancies between the experimental and calculated quantities are unbiased and they appear globally for solvents with varied extents. Attempts of interpreting such differences have been made for H$_2$O, particularly in UV range, $^{42-44, 47}$ however the conceived explanations are not viable to account for the striking disagreements observed for H$_2$O in visible and other solvents across a wider wavelength. These results might suggest that Einstein-Smoluchowski equation is not complete yet to exactly compute the light scattering of solvents.
As shown in Figure 5, in comparison to the pair solvents of H₂O and D₂O, the flat and pronounced extinctions spanning across the visible spectral range were observed for the solvents of DMSO and DMSO-d₆. An easily-raised query is about whether these anomalous extinctions of DMSO and DMSO-d₆ are from the superposition and continuum of many overtones (and combination bands) therein. First, the harmonics in the shorter wavelengths (e.g., < 736 nm for DMSO, and < 1001 nm for DMSO-d₆) are supposed to be very weak due to the orders of magnitude reduction compared to the fundamental resonances. Second, the difference of experimental and computed results remains evident from 350-400 nm where the light scattering takes the dominance and the vibration-induced absorption is negligible (given the UV cut-off wavelength of DMSO at about 268 nm, the contribution of absorption from electronic transition is excluded.). Third, for the same wavelength, the extinction of DMSO in visible is principally expected to be one order of larger than that of DMSO-d₆, by simply summing up the extinctions from the harmonics and light scattering computed by Einstein’s equation, which, however, contradicts with the experimental observation. The only explanation to these facts is likely that the full terms contributing to the light scattering are not entirely included into Einstein-Smoluchowski equation. Such unidentified scattering terms are solvent-dependent, because of (1) forming the V-groove extinctions for H₂O and D₂O but the flare-groove extinctions for DMSO and DMSO-d₆ and (2) the scattering of DMSO and DMSO-d₆ much more pronounced than that of H₂O and D₂O. All above suggest that the assumption of that the rehabilitated Einstein-Smoluchowski equation is not completely sufficient to retrieve the light scattering of solvent should hold, i.e., the ultimate equation/theory to compute the light scattering of solvent is still pending.

In this work, we develop the “Four-step measurement method” to determine the extinction coefficients of solvents with high accuracy and high confidence. By only using the 0.5 cm differential path length and the standard double-beam spectrophotometer, we have,
theoretically and experimentally, demonstrated that the strong viability of our methodology (at the level of $10^{-4}$ dB/cm) and confirmed its limit just lies in the instrumental characteristics. By revisiting the various equations widely used to compute the scattering of solvent, we rehabilitate Einstein-Smoluchowski initial equation, which shows the closest approximation to experimental observations as well as offers the high simplicity and predictability in use. Our research further demonstrates that the use of Einstein-Smoluchowski equation remain insufficient to fully retrieve the light scattering of solvent, which expects to inspire a renaissance of studies (experimental and theoretical) in this field. To this end, we suggest the studies shall extend from the challenging candidates of H₂O to other solvents with high extinctions, e.g., DMSO, by empirically obtaining their absorption and extinction coefficients. The techniques and knowledge advanced in this work could be advantageous for a large variety of research and applications, e.g., making the appropriate option about the liquid media for state-of-the-art optofluidics devices, quantifying the exact extinctions of liquid-based laser media, and evaluating the quality of H₂O with significant capital cost reduction for different industrial uses as well as benefiting to the scientific work on the still mysterious structure of liquid H₂O.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ....

Materials and methods, supporting figures and tables, and additional references (PDF)

AUTHOR INFORMATION
Notes

The authors declare no competing financial interests.

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REFERENCES

1. Rayleigh, L., XXXIV. On the transmission of light through an atmosphere containing small particles in suspension, and on the origin of the blue of the sky. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 1899, 47 (287), 375-384.
2. Kreusler, H., Anwendung des photoelektrischen Stromes zur Photometrie der ultravioletten Strahlen. Annalen der Physik 1901, 311 (10), 412-423.
3. v. Smoluchowski, M., Molekular-kinetische Theorie der Opaleszenz von Gasen im kritischen Zustande, sowie einiger verwandter Erscheinungen. Annalen der Physik 1908, 330 (2), 205-226.
4. Raman, C. V., On the molecular scattering of light in water and the colour of the sea. Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character 1922, 101 (708), 64-80.
5. Einstein, A., Theory of opalescence of homogenous liquids and liquid mixtures near critical conditions. Annalen Der Physik 1910, 33 (16), 1275-1298.
6. Debye, P., Light scattering in solutions. Journal of Applied Physics 1944, 15 (4), 338-342.
7. Prins, W., LIGHT SCATTERING BY AQUEOUS SUCROSE SOLUTIONS. The Journal of Physical Chemistry 1961, 65 (2), 369-370.
8. Coumou, D.; Mackor, E., Isotropic light-scattering in binary liquid mixtures. Transactions of the Faraday Society 1964, 60, 1726-1735.
9. Kratothvil, J.; Kerker, M.; Oppenheimer, L., Light scattering by pure water. The Journal of Chemical Physics 1965, 43 (3), 914-921.
10. Hale, G. M.; Querry, M. R., Optical constants of water in the 200-nm to 200-μm wavelength region. Applied optics 1973, 12 (3), 555-563.
11. Boivin, L.-P.; Davidson, W.; Storey, R.; Sinclair, D.; Earle, E., Determination of the attenuation coefficients of visible and ultraviolet radiation in heavy water. Applied optics 1986, 25 (6), 877-882.
12. Pope, R. M.; Fry, E. S., Absorption spectrum (380–700 nm) of pure water. II. Integrating cavity measurements. Applied optics 1997, 36 (33), 8710-8723.
13. Zhang, X.; Hu, L., Estimating scattering of pure water from density fluctuation of the refractive index. Optics express 2009, 17 (3), 1671-1678.
14. Mason, J. D.; Cone, M. T.; Fry, E. S., Ultraviolet (250–550 nm) absorption spectrum of pure water. Applied optics 2016, 55 (25), 7163-7172.
15. Marin, T. W.; Janik, I.; Bartels, D. M.; Chipman, D. M., Vacuum ultraviolet spectroscopy of the lowest-lying electronic state in subcritical and supercritical water. Nature communications 2017, 8, 15435.
16. Groh, W., Overtone absorption in macromolecules for polymer optical fibers. Die Makromolekulare Chemie: Macromolecular Chemistry and Physics 1988, 189 (12), 2861-2874.
17. Irikura, K. K., Experimental vibrational zero-point energies: Diatomic molecules. Journal of physical and chemical reference data 2007, 36 (2), 389-397.
18. Wallace, V. M.; Dhumal, N. R.; Zehentbauer, F. M.; Kim, H. J.; Kiefer, J., Revisiting the aqueous solutions of dimethyl sulfoxide by spectroscopy in the mid-and near-infrared: experiments and Car–Parrinello simulations. The Journal of Physical Chemistry B 2015, 119 (46), 14780-14789.
19. Kao, K.; Hockham, G. A. In Dielectric-fibre surface waveguides for optical frequencies, Proceedings of the Institution of Electrical Engineers, IET: 1966; pp 1151-1158.
20. Abe, K.; Hayato, Y.; Iida, T.; Ikeda, M.; Ishihara, C.; Iyogi, K.; Kameda, J.; Kobayashi, K.; Koshio, Y.; Kozuma, Y., Solar neutrino results in Super-Kamiokande-III. Physical Review D 2011, 83 (5), 052010.
21. Wang, Y.; Wen, W.; Wang, K.; Zhai, P.; Qiu, P.; Wang, K., Measurement of absorption spectrum of deuterium oxide (D2O) and its application to signal enhancement in multiphoton microscopy at the 1700-nm window. Applied Physics Letters 2016, 108 (2), 021112.
22. Otanicar, T. P.; Phelan, P. E.; Golden, J. S., Optical properties of liquids for direct absorption solar thermal energy systems. Solar Energy 2009, 83 (7), 969-977.
23. Lee, S. J.; Morrill, A. R.; Moskovits, M., Hot spots in silver nanowire bundles for surface-enhanced Raman spectroscopy. J Am Chem Soc 2006, 128 (7), 2200-2201.
24. Abe, H.; Manzel, K.; Schulze, W.; Moskovits, M.; Dilella, D. P., Surface-Enhanced Raman-Spectroscopy of Co Adsorbed on Colloidal Silver Particles. J. Chem. Phys. 1981, 74 (2), 792-797.
25. Damasiewicz, M. J.; Polkinghorne, K. R.; Kerr, P. G., Water quality in conventional and home haemodialysis. Nature Reviews Nephrology 2012, 8 (12), 725.
26. Vezenov, D. V.; Mayers, B. T.; Conroy, R. S.; Whitesides, G. M.; Snee, P. T.; Chan, Y.; Nocera, D. G.; Bawendi, M. G., A low-threshold, high-efficiency microfluidic waveguide laser. Journal of the American Chemical Society 2005, 127 (25), 8952-8953.
27. Fan, X.; Yun, S.-H., The potential of optofluidic bioslasers. Nature methods 2014, 11 (2), 141.
28. Chemnitz, M.; Gaida, C.; Gebhardt, M.; Stutzki, F.; Kobelke, J.; Tünnermann, A.; Limpert, J.; Schmidt, M. A., Carbon chloride-core fibers for soliton mediated supercontinuum generation. Opt. Exp. 2018, 26 (3), 3221-3235.
29. Chemnitz, M.; Gebhardt, M.; Gaida, C.; Stutzki, F.; Kobelke, J.; Limpert, J.; Tünnermann, A.; Schmidt, M. A., Hybrid soliton dynamics in liquid-core fibres. Nat Commun 2017, 8 (1), 42.
30. Jones, M.; Kao, K., Spectrophotometric studies of ultra low loss optical glasses ii: double beam method. Journal of Physics E: Scientific Instruments 1969, 2 (4), 331.
31. Suh, J. S.; Dilella, D. P.; Moskovits, M., Surface-Enhanced Raman-Spectroscopy of Colloidal Metal Systems - a Two-Dimensional Phase-Equilibrium in Para-Aminobenzoic Acid Adsorbed on Silver. J Phys Chem-Us 1983, 87 (9), 1540-1544.
32. Segelstein, D. J. The complex refractive index of water. University of Missouri-Kansas City, 1981.
33. Sullivan, S. A., Experimental study of the absorption in distilled water, artificial sea water, and heavy water in the visible region of the spectrum. JOSA 1963, 53 (8), 962-968.
34. Kedenburg, S.; Vieweg, M.; Gissibl, T.; Giessen, H., Linear refractive index and absorption measurements of nonlinear optical liquids in the visible and near-infrared spectral region. Optical Materials Express 2012, 2 (11), 1588-1611.
35. Rao, P. V.; Fink, R. W., Neutron Reaction Cross Sections of Selenium and Iron at 14.4 Mev. Phys. Rev. 1967, 154 (4), 1023-8.
36. Etchegoin, P. G.; Le Ru, E. C.; Meyer, M., An analytic model for the optical properties of gold. J. Chem. Phys. 2006, 125 (16), 164705.
37. Oh, K. I.; Rajesh, K.; Stanton, J. F.; Baiz, C. R., Quantifying Hydrogen-Bond Populations in Dimethyl Sulfoxide/Water Mixtures. Angewandte Chemie 2017, 129 (38), 11533-11537.
38. Plidischun, M.; Chemnitz, M.; Schmidt, M. A., Low-loss deuterated organic solvents for visible and near-infrared photonics. Optical Materials Express 2017, 7 (4), 1122-1130.
39. Kaino, T., Preparation of plastic optical fibers for near-IR region transmission. Journal of Polymer Science Part A: Polymer Chemistry 1987, 25 (1), 37-46.
40. Farinato, R. S.; Rowell, R. L., New values of the light scattering depolarization and anisotropy of water. The Journal of Chemical Physics 1976, 65 (2), 593-595.
41. Weber, M. J., Handbook of optical materials. CRC press: 2018.
42. Quickenden, T.; Irvin, J., The ultraviolet absorption spectrum of liquid water. The Journal of Chemical Physics 1980, 72 (8), 4416-4428.
43. Kröckel, L.; Schmidt, M. A., Extinction properties of ultrapure water down to deep ultraviolet wavelengths. *Optical Materials Express* **2014**, *4* (9), 1932-1942.

44. Marin, T. W.; Takahashi, K.; Bartels, D. M., Temperature and density dependence of the light and heavy water ultraviolet absorption edge. *The Journal of Chemical Physics* **2006**, *125* (10), 104314.

45. Pegau, W. S.; Gray, D.; Zaneveld, J. R. V., Absorption and attenuation of visible and near-infrared light in water: dependence on temperature and salinity. *Applied optics* **1997**, *36* (24), 6035-6046.

46. McGowan, J., The isothermal compressibilities of liquids. *Recueil des Travaux Chimiques des Pays-Bas* **1957**, *76* (2), 155-164.

47. Litjens, R. A.; Quickenden, T. I.; Freeman, C. G., Visible and near-ultraviolet absorption spectrum of liquid water. *Applied optics* **1999**, *38* (7), 1216-1223.
Science of light scattering of solvent undergoes evolution: improved spectrophotometric measurement rehabilitates Einstein-Smoluchowski equation

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Table S1. Summary of the extinctions of H₂O from near UV to NIR measured by spectrophotometers at room temperature. The table supplements the review by Ref. [1] which provided a wide coverage of previous works from 1891-1997.

| Year | Method       | Instrumental                  | Differential path length (cm) | Mean % diff. \(^a\) | Refs. |
|------|--------------|--------------------------------|-------------------------------|----------------------|-------|
| 1934 | Single-beam  | Customer-designed photographic photometer | 272                           | \(~ 61\) \(^b\)     | [2]   |
| 1963 | Single-beam  | Customer-designed spectrophotometer | 132                           | \(~ 17\) \(^c\)     | [3]   |
| 1986 | Single-beam  | Customer-designed spectrophotometer | 50.3                          | \(~ 55\) \(^d\)     | [4]   |
| 1999 | Single-beam  | Customer-designed spectrophotometer | 150                           | \(~ 2.1\) \(^e\)    | [5]   |
| 2009 | Double-beam  | Commercial spectrophotometer      | 0.9                           | \(~ 9900\)          | [6]   |
| 2012 | Single-beam  | Customer-designed spectrophotometer | 100                           | \(~ 105\) \(^f\)    | [6]   |
| 2015 | Double-beam  | NA                              | 5                             | \(~ 181\)           | [7]   |
| 2017 | Single-beam  | Customer-designed ellipsometer    | 20                            | \(~ 323\)           | [8]   |
| 2019 | Double-beam  | Commercial spectrophotometer       | 0.5                           | \(~ -22\)           | This work |

\(^a\) The mean % diff. = \(100\% \times (\text{Exp}_1 - \text{Exp}_2)/\text{Exp}_2\), where \(\text{Exp}_2\) denotes the extinction coefficient of H₂O at 480 nm by Segelstein \(^9\) (used as a benchmark data), and \(\text{Exp}_1\) stands for the values obtained by others.

\(^b,c\) The calculation refers to the wavelength of 400 nm as the extinction of 480 nm is too low to be measured.

\(^d\) The calculation refers to the wavelength of 436 nm as the data at 480 nm is not provided.
The calculation refers to the wavelength of 400 nm, since at 480 nm, the extinction coefficient was observed with the minus mean value.

The calculation refers to the starting wavelength of 500 nm.

Table S2. The tabulated parameters of H$_2$O, D$_2$O, DMSO, and DMSO-d$_6$ used for the computation of the light scattering of solvents at room temperature, as well as the theoretically and experimentally obtained scattering/extinction coefficients of solvents for comparison. Unless specified, the properties of solvents are denoted at wavelengths as follows, H$_2$O at 344 nm, D$_2$O at 650 nm, and both DMSO and DMSO-d$_6$ at 500 nm. For H$_2$O, the experimental scattering coefficient $\tilde{b}$ is given, and for the others, the experimental extinction coefficients $\tilde{\mu}$ are provided due to the lack of their absorption coefficients.

|        | $\Delta$ | $\beta_T \times 10^{-10}$ | $\gamma \times 10^{-18}$ | $n^f$ | $\tilde{b}$ or $\tilde{\mu} \times 10^{-4}$ | $\%$ diff. $^g$ |
|--------|----------|--------------------------|--------------------------|-------|-----------------------------------------------|------------------|
|        |          | m$^2$/N                   | mN/m                     |       | dB/cm (Exp)                                   | dB/cm (Eq. 7&8)  |
| H$_2$O | 0.108 $^a$ | 4.58 $^{10}$              | 71.98 $^{11}$            | 1.35008 | 7.71                                          | 5.93             | 30          |
| D$_2$O | 0.111 $^b$ | 4.74 $^{12}$              | 71.87 $^{13}$            | 1.33243 | 4.30                                          | 0.43             | 900         |
| DMSO   | 0.436 $^c$ | 5.32 $^{10}$              | 43.54 $^{14}$            | 1.48194 | 317.8                                         | 8.70             | 3553        |
| DMSO-d$_6$ | 0.439 $^d$ | 5.28 $^e$                 | 43.7 $^{15}$             | 1.47801 | 197.6                                         | 8.41             | 2250        |

$^a$ The value of $\Delta$ of H$_2$O is from the average quantities of all measurements. $^{16}$

$^b$ The net difference of $\Delta$ between D$_2$O and H$_2$O is 0.003. $^{17}$

$^c$ The value was extrapolated by a polynomial fitting of $\Delta$ of DMSO in the temperature range 30-48 °C ($R^2=1$), $^{18}$ in good agreement with structurally similar solvent Dimethylformamide (DMF, $\Delta=0.453$)$^{19}$.

$^d$ The value was estimated via the same net difference between regular and deuterated solvents as $^b$.

$^e$ None numerical value was found for DMSO-d$_6$ after a thorough literature search. The listed value here was calculated in accordance with $\beta_T \gamma^{7/4} = \text{constant}$, where the constant is the same for DMSO and DMSO-d$_6$ (the nearly equality of the product is also found for H$_2$O and D$_2$O).
All refractive indices \( n \) of solvents noted were given for at 25 °C. Since \( n \) varies at the fourth digit between 20-25 °C, e.g., < 0.0005 for \( \text{H}_2\text{O} \), the set of index data at this temperature can be used to evaluate the scattering coefficient of solvents at room temperature.

\[
\% \text{ diff.} = \frac{\text{Exp} - \text{Cal}}{\text{Cal}}, \text{ where Exp is the experimental quantity and Cal is the computed value of the coefficient.}
\]

**Section S1. Experimental preparation and instrumental evaluation**

The determination of the extinction coefficient of a solvent is not an easy task. The experimental procedures pertinent to this study are thus enumerated in detail.

**S1.1 Solvent samples**

Ultrapure \( \text{H}_2\text{O} \) was supplied by a SG Ultra Clear UV plus TM / EI-Ion® system, which dispenses ultrapure \( \text{H}_2\text{O} \) with a resistivity of 18.2 M\( \Omega \)-cm and a total organic carbon (TOC) level < 1 ppb. Deuterated water (\( \text{D}_2\text{O}, 99.9 \) atom % D), dimethyl sulfoxide (DMSO for spectroscopy, purity \( \geq 99.8 \) %) and deuterated DMSO (DMSO-\( \text{d}_6 \), 99.9 atom % D) were purchased from Sigma-Aldrich and used without further purification. All solvents were prepared freshly (< 30 min) with great care prior to the spectrophotometric measurements.

High-purity solvents are leaching substances, particularly ultrapure \( \text{H}_2\text{O} \). To reduce the impurities leached by the solvents that they are in contact with, pre-cleaned glass vials (Pyrex glass with PTFE/silicone septum) were used to store and transfer the solvents.

**S1.2 Cuvette cells**

In addition to the use as a solvent container, the cuvette cells inserted in the compartments are considered as the essential optical component of the spectrophotometer. Thus, the cells used must be of quality and flawless.

In our experimental setup, Brand-new Hellma 110-QS Quartz Glass cells (high performance, 200-2500 nm) of 0.5 and 1.0 cm path lengths (tolerance accuracy ± 0.001 cm) were
purchased. Only the blank cells giving consistent and reproducible transmissions > 80 % from 200-2500 nm during multiple removal and re-insertion operations (against air as a reference substance) were picked up for the following measurements. In the subsequent process of handling and cleaning these selected cuvettes, the extreme care was taken to avoid any damages induced.

**S1.3 Cleaning procedures**

To prevent the measurement errors from impurities and contaminations, only the ultra-clean containers, e.g., glass vials and cuvette cells, were used. To this end, all glass vials, cuvette cells, and PTFE lids were immersed in a ~ 2% (v/v) Hellmanex III cleaner solution for about 30 min, followed by an ultrasonication < 5 min at moderate temperature (to accelerate the cleaning process). These parts were subsequently rinsed thoroughly by flowing ethanol, distilled H2O, and ultrapure H2O in sequence. Note that, to effectively leach away the residual impurities, such as absorbed contaminants and particulates, ultrapure H2O was used for rinsing in the last step, due to its corrosive characteristic. All the cleaned components were dried by purging N2, for immediate use or storage in a desiccator (to avoid airborne contaminants).

**S1.4 Spectrophotometric measurement**

To attain the reliable spectrophotometric measurements for the wavelength range 350-1400 nm, the standard double beam, scanning Spectrophotometers JASCO V-660 (working wavelength 187-900 nm) and V-670 (working wavelength 190-2700 nm) were both employed in this work, at different spectral regions (details provided in the sub-section of S1.5). A spectra resolution of 0.5 nm with a scanning speed of 100 nm/min and medium response was chosen throughout all measurements, by which the stable baseline characteristic, good signal to noise ratio and spectra shape could be assured. The bandwidth was set as 2 nm for the wavelength range < 900 nm, and 8 nm for that > 900 nm. The instrument was warmed up >
60 mins for a sufficient thermal equilibrium. The change wavelength for V-670 was set at 900 nm for both the grating and detector. The baseline correction was carried out via spectrophotometric scan of air in both sample and reference channels.

**S1.5 Instrumental capacity – baseline flatness and absorbance stability**

The instrumental imperfection is unavoidable for the spectrophotometer. This makes the photon flux densities of the dual beams differ slightly upon the detector (i.e., the unequal photocurrents). To eliminate the photocurrent difference as well as obtain the null current relevant to the two beams, the baseline correction is, therefore, carried out, i.e., declaring the zero absorbance in measurements of the reference substance.

With the record of the null current, the absorbance of the sample of interest is accounted relative to this "zeroed" substance, i.e., the resultant absorbance obtained by the subtraction of the (memorized) baseline datum from the measured values.

According to above concisely-described working principle of a spectrophotometer, its capacity, including the accuracy, precision and detection limit, could be largely related to the baseline characteristic, e.g., baseline flatness (known as instrumental noise) and baseline drift (known as absorbance stability).

**Baseline flatness (instrumental noise)**

The baseline flatness is quoted as the value of standard deviation (SD) of multiple “zero” absorbance where air substance is used in the both reference and sample compartments.

In spite of the baseline flatness of ± 0.0005 Abs specified for both spectrophotometers by the manufacturer over the wavelength range from 200 to 800 nm, their noise levels are re-examined in this work. This is because that the instrumental noise may differ due to the possible variations of light sources, instrumental and detector characteristics in the broader wavelengths.
To ensure the evaluation of the instrumental noise with the suppressed statistical bias, six spectrophotometric scans were conducted. To exclude the perturbation of baseline drift (as discussed below), the baseline scan was only exercised after “zero” absorbance measurement. In accordance with the equation of SD, the instrumental noises were calculated and shown in Figure S1. It shows that the noises of V-660 fluctuate between ± 0.00003 Abs from 350-650 nm and ± 0.00005 Abs from 650-800 nm, and its noise increases up to ± 0.001 Abs from 800-900 nm, resulting from the suffered sensitivity of photomultiplier tube (PMT) above 800 nm (Figure S1a). The noises of V-670 are stabilized within ± 0.00003 Abs from 350-850 nm, but decently increasing to ± 0.0004 Abs in between 850-950 nm where the detectors and filters are changed (e.g., PMT switching to PbS photoconductive cell), followed by a slight decrease to ± 0.0002 Abs in the wavelength from 950-1400 nm (Figure S1b). Those results suggest that, with regard to the instrumental noise, the spectrophotometers of V-660 and V-670 are interchangeable in the wavelengths concerned in this work.

![Figure. S1 Instrumental noise of Spectrophotometers V-660 (a) and V-670 (b) across the wavelengths noted, which were obtained according to the SD equation in the mean of six separate scans.](image-url)
**Baseline drift (absorbance stability)**

Due to the filters switching, light sources exchanges, etc, the baseline of a spectrophotometer differ slightly over a series of scans even upon the identical parameters (this is called baseline drift). Given that the measured absorbance is accounted relative to the initially-recorded baseline but the real absorbance refers to the on-going baseline datum, the discrepancy between the measured absorbance and the real absorbance of a substance should exist and escalates over multiple scans. To define the accuracy of a spectrophotometer, the degrees of the baseline drift as a function of scanning time must be known.

**Figure. S2** Characterizations of baseline drift of Spectrophotometers V-660 (a) and V-670 (b). Following one baseline correction scan with a series of “zero” absorbance measurements over times, the net difference $\Delta$Abs of air substance in different time intervals was obtained by equation $\Delta$Abs = $|$Abs$_{t1}$ – Abs$_{t2}$|, where Abs$_{t1/2}$ denotes the absorbance measured at $t_1$ and $t_2$, respectively.

To evaluate the baseline drift of spectrophotometers used in this study, six “zero” absorbance measurements were sequentially conducted relative to only once baseline correction scan. This is in stark contrast to the study of the baseline flatness where multiple baseline corrections were performed prior to each spectrophotometric scan. As shown in Figure S2a, the baseline drift of V-660 over a period of 60 minutes is negligible from 350-900 nm, i.e., $|A_{t0} – A_{t10}| = |A_{t0} – A_{t60}|$. In Figure S2b, the baseline drift of V-670 is not detectable from 850-
1400 nm over the period of observation, which stands in contrast to the progressive drifts observed from 350-850 nm, i.e., < 0.00001 Abs/12 min versus 0.00005~0.0004 Abs/72 min. As such, V-660 and V-670 are used in a combination manner for the best performance in the wavelengths from 350-850 nm and 850-1400 nm, respectively.

With a scanning speed of 100 nm/min, about 5 and 5.5 min per scan are taken for V-660 (350-850 nm) and V-670 (850-1400 nm). For “Four-step measurement method”, four spectrophotometric scans per sample are needed to accomplish the extinction measurement, i.e., about 22 min taken by each spectrophotometer for the scan of wavelengths concerned. As shown in Figure S2, the baseline drifts are negligible over 22 min; even the baseline drifts exist, they are all within the range of the instrument noises. This attests that the combined use of spectrophotometers allows to attain the highest accuracy that can be accessed.

By setting the signal to noise ratio (SNR) 2:1 as a threshold (2σ) for a reliable data acquisition, the combined use of the spectrophotometers in different wavelengths make the instrumental detection limit 0.00006 Abs (from 350-850 nm), ~ 0.0008 Abs (from 850-950 nm), and < 0.0004 Abs (from 950-1400 nm).

**Section S2. Optics in spectrophotometric measurement**

**S2.1 Beer-Lambert law**

According to Beer-Lambert law, the absorbance \( A \), so-called extinction) and the transmittance \( T_t \) of light traversing through a medium are given by:

\[
A = -\log_{10} \left( \frac{I_t}{I_0} \right) = -\log_{10} T_t = \mu L
\]  

(1)

where \( I_0 \) and \( I_t \) are the radiant flux of the incident and transmitted light, respectively, \( \mu \) the decadic extinction coefficient of a medium (unit: cm\(^{-1}\)), and \( L \) the light path length. The
decadic extinction coefficient $\mu$ can be converted into the extinction coefficient $\tilde{\mu}$ with unit dB/cm, via a relation of $\tilde{\mu} = 10\mu$.

In this paper, $\tilde{\mu}$ or $\mu$ is used as a quantitative measure to the extinction of a solvent per unit length. For the sake of convenient comparison, the extinctions given in napierian form in literatures are converted into the decadic expression by a factor $1/Ln10$.

The extinction coefficient ($\mu$ or $\tilde{\mu}$) is the sum of the absorption coefficient ($a$ or $\tilde{a}$) and the scattering coefficient ($b$ or $\tilde{b}$), which is written as:

\[
\mu = a + b \quad \text{or} \quad \tilde{\mu} = \tilde{a} + \tilde{b}. \quad (2)
\]

S2.2 Optical paths in cuvette

Little experimental efforts would be taken to obtain an extinction spectrum of solvent by inserting the empty and solvent-filled cuvette cells in the spectrophotometer. However, to correctly extract the extinction coefficients, the complexity and difference of optical paths that a ray of light would undergo in the empty and solvent-filled cells must be acknowledged.

\[I_0(T_{\text{air},500}, T_{\text{sol}}) \times T_i \times (R_{\text{air},500}T_{\text{sol}})^2 \]

\[I_0(T_{\text{air},500}, T_{\text{sol}}) \times T_i \times (R_{\text{air},500}T_{\text{sol}})^2 \]

\[I_0(T_{\text{air},500}, T_{\text{sol}}) \times T_i \times (R_{\text{air},500}T_{\text{sol}})^2 \]

\( \text{Figure. S3} \) Schematic diagrams of the transmitted light exiting from the liquid-filled (a) and empty (b) cuvettes, respectively. The schematics illustrate the resultant transmitted flux containing the light that undergoes multiple reflections, refractions, and transmissions at the relevant interfaces and/or over the mediums. For visualization, the components that transverse the medium (either air or liquid) once and thrice are sketched with intention of normal incidence.
**Liquid-filled cuvette**

As illustrated in Figure S3a, the total transmitted light passing through a liquid-filled cuvette is constituted as:

\[
I_{t,f} = I_0 \left( T_{\text{air}, \text{SiO}_2} T_{\text{SiO}_2} \right)^2 T_i \left( 1 + \frac{1}{\text{once medium transverse}} \right) + \frac{R_{\text{air}, \text{SiO}_2}^2 T_{\text{SiO}_2}^2}{\text{thrice medium transverses}} + \frac{R_{\text{air}, \text{SiO}_2}^4 T_{\text{SiO}_2}^2 T_i^2}{\text{five times medium transverses}} + \cdots \tag{3}
\]

For the wavelengths concerned, \( R_{\text{air}, \text{SiO}_2} \) is smaller than 0.037, the respective transmittance of air \( T_{\text{air}} \) and cuvette glass \( T_{\text{SiO}_2} \) essentially approximating to unity, and \( T_i \) always below 1, hence the infinite series can be summed and simplified to:

\[
I_{t,f} = I_0 \left( T_{\text{air}, \text{SiO}_2} T_{\text{SiO}_2} \right)^2 T_i \left( 1 + \delta_f \right) \tag{4}
\]

where \( \delta_f \) is in the approximation to 0.001\( T_i^2 \).

**Empty cuvette**

As shown in Figure S3b, for the empty cuvette with air as a medium, in addition to the first-order transmitted light, the reflected light at each air-glass interfaces would pass through the medium once, thrice, and so on, and air-glass interface for six, eight times, etc, to yield the higher-order transmitted light. The total transmitted light is thus written as:

\[
I_{t,e} = I_0 \left( T_{\text{air}, \text{SiO}_2} T_{\text{SiO}_2} \right)^2 T_{\text{air}} \left( 1 + 2R_{\text{air}, \text{SiO}_2}^2 T_{\text{SiO}_2}^2 \right) + \frac{R_{\text{air}, \text{SiO}_2}^2 T_{\text{air}}^2}{\text{once medium transverse}} + \frac{2R_{\text{air}, \text{SiO}_2}^2 T_{\text{air}, \text{SiO}_2} T_{\text{air}} T_{\text{SiO}_2}^2 T_i^2}{\text{thrice medium transverses}} + \frac{R_{\text{air}, \text{SiO}_2}^4 T_{\text{air}, \text{SiO}_2} T_{\text{air}} T_{\text{SiO}_2}^4 T_i^4}{\cdots} \tag{5}
\]
Applying the same simplification, the summed amount of the transmitted light is given by:

\[ I_{t,e} = I_0 (T_{\text{air}, \text{SiO}_2}^2 T_{\text{SiO}_2}^2) T_{\text{air}} (1 + \delta_e), \quad (6) \]

where \( \delta_e \) is approximately 0.007.

In our analysis, besides the first-order transmitted light, the higher-order transmissions \( I_0 (T_{\text{air}, \text{SiO}_2}^2 T_{\text{SiO}_2})^2 T_i \delta_f \) and \( I_0 (T_{\text{air}, \text{SiO}_2}^2 T_{\text{SiO}_2})^2 T_{\text{air}} \delta_e \) are taken into account for liquid-filled and empty cuvettes, respectively. Though their quantities are minor, the omission of these trivia should be avoided. Otherwise, the key criteria of using cuvettes throughout the measurements is hidden, i.e., a pair of cells in use must be as much as possible clean, quality, and identical, which actually is the decisive factor for a successful measurement (as discussed below).

**Section S3. Four-step measurement method**

**S3.1 Experimental operations**

The “Four-step measurement method” involves the wavelength scans of the empty and liquid-filled cuvettes in a sequential manner, during which each cuvette is only placed in the sample compartment in accompany with air as the reference substance in the adjacent compartment.

The measurement operations were exercised as follow in order: a baseline correction \( \rightarrow \) absorbance measurement of a short-length empty cuvette in insertion (step 1) \( \rightarrow \) filling the solvent without removing or touching the cuvette, followed by a spectrophotometric scan (step 2) \( \rightarrow \) replacing with a long-length empty cuvette and conducting another absorbance measurement (step 3) \( \rightarrow \) filling the solvent in the long-length cuvette followed with the last scan (step 4). It is worthwhile to note that the cuvettes are retained immobile completely.
through the whole operations, including filling the solvent; this enables to minimize the experimental uncertainties.

S3.2 Theoretical derivation

For the light beam from a stable lamp source supplied with a regulated DC power, the incident light $I_0$ is considered to be invariant. For the selected cuvettes, they nearly holds the equality, i.e., the same $n_{SiO_2}$ and $T_{SiO_2}$ for the cuvettes, which allows to conveniently cancel out the unknown terms related to the cuvettes used.

As long as above conditions are true, the substitution of Eqs. (S4) and (S6) of the incident light $I_0$ and the transmitted light of $I_{L1,e,s}$, $I_{L1,f,s}$, $I_{L2,e,s}$, and $I_{L2,f,s}$ into Eq. S1 gives:

$$\Delta A_{L1,s} = A_{L1,f,s} - A_{L1,e,s}$$

$$= -\log_{10}\left(\frac{T_{L1,f,s}}{T_{air,SiO_2}^2 T_{air}} \frac{1 + \delta_{L1,f,s}}{1 + \delta_{L1,e,s}}\right)$$

and

$$\Delta A_{L2,s} = A_{L2,f,s} - A_{L2,e,s}$$

$$= -\log_{10}\left(\frac{T_{L2,f,s}}{T_{air,SiO_2}^2 T_{air}} \frac{1 + \delta_{L2,f,s}}{1 + \delta_{L2,e,s}}\right).$$

Subtraction between Eqs. (S8) and (S7) derives the expression of $\mu$ as:

$$\mu = \frac{\Delta A_{L2,s} - \Delta A_{L1,s}}{L_2 - L_1} + \frac{Y}{L_2 - L_1}$$

and $Y$ is described as:

$$Y = \log_{10}\left(\frac{1 + \delta_{L2,f,s}}{1 + \delta_{L1,e,s}}\right) = \log_{10}\left(\frac{1 + \delta_{L2,f,s}}{1 + \delta_{L1,f,s}}\right).$$

Eqs. (S9) and (S10) are the mathematical expression of the Four-step measurement.
For a pseudo solvent with the extinction coefficient in the range from 0.00001 to 0.1 cm$^{-1}$ ($L_1=0.5$ cm and $L_2=1.0$ cm), $Y/(L_2 - L_1)$ varies from $-2.0 \cdot 10^{-8}$ to $-1.4 \cdot 10^{-4}$ cm$^{-1}$, leading to errors between $-0.20\%$ $\sim$ $-0.14\%$, respectively.

These above suggest, when the terms relevant to cuvettes are cancelled out and $Y$ is inconsiderable to be accounted, high-accuracy $\mu$ (and $\bar{\mu}$) can be readily derived via Eq. (S9) by measuring $A_{t1,s}, A_{t1,f,s}, A_{t2,e,s}, A_{t2,f,s}$ of the cuvettes with defined lengths of $L_1$ and $L_2$.

S3.3 Theoretical derivation of conventional Two-step measurement method

Using the similar derivation process as did for Four-step measurement, we obtained the formulation used for extracting the extinct coefficient of a solvent based upon “Two-step method” as:

$$
\mu = \frac{A_f - A_e}{L_{2,s} - L_{1,r}} + 2\log_{10} \left( \frac{T_{air, SiO_2, L_{2,s}}}{T_{air, SiO_2, L_{1,r}}} \right) + \frac{Y}{L_{2,s} - L_{1,r}},
$$

(11)

where $A_f = \log_{10} \frac{l_{t,f,L_{1,r}}}{l_{t,f,L_{2,s}}}, A_e = \log_{10} \frac{l_{t,e,L_{1,r}}}{l_{t,e,L_{2,s}}}$, and $Y$ is described as:

$$
Y = \log_{10} \left( \frac{1 + \delta_{L_{1,f},r} 1 + \delta_{L_{2,e},s}}{1 + \delta_{L_{2,f},s} 1 + \delta_{L_{1,e},r}} \right).
$$

(12)

The Eq. (S11) suggests its second and third items cannot be directly eliminated due to the differences of beams between the sample ($s$) and reference ($r$) channels for different length cuvettes ($L_1$ and $L_2$). With the insertion of cuvettes, the escalated differences of the beams in these two channels would increasingly deviate the (measured) extinction coefficient from the real value.
Section S4. Compilation of experimental uncertainties

S4.1 Theoretical compilation of experimental uncertainties

As discussed, the extinction coefficient of solvent is derived based on the four absorbance measurements. Given ignoring the inconsiderable item $Y$ in Eq. (S9), a propagation of error of the variables yields the uncertainty of the extinction coefficient as:

$$ S_{\mu}^2 = \left( \frac{1}{L_2 - L_1} \right)^2 S_{(\Delta A_{L_2,s} - \Delta A_{L_1,s})}^2 + \frac{(\Delta A_{L_2,s} - \Delta A_{L_1,s})^2}{(L_2 - L_1)^4} S_{(L_2 - L_1)}^2 $$

$$ - 2 \frac{\Delta A_{L_2,s} - \Delta A_{L_1,s}}{(L_2 - L_1)^3} S_{AL_s} $$

where

$$ S_{(\Delta A_{L_2,s} - \Delta A_{L_1,s})}^2 = S_{A_{L_2,f,s}}^2 + S_{A_{L_2,e,s}}^2 + S_{A_{L_1,f,s}}^2 + S_{A_{L_1,e,s}}^2 $$

$$ S_{(L_2 - L_1)}^2 = S_{L_2}^2 + S_{L_1}^2 $$

Since the sum of the cross term $S_{AL}$ approaches zero, it is not mathematically expressed.

The standard deviation of the absorbance, $S_A$, is described as (ignoring a possible covariance between $\theta$, $L$ and $n$):

$$ S_A^2 = \left( \frac{\partial A}{\partial L} \right)^2 S_L^2 + \left( \frac{\partial A}{\partial \theta} \right)^2 S_{\theta}^2 + \left( \frac{\partial A}{\partial n_{SiO_2}} \right)^2 S_{n_{SiO_2}}^2 $$

(16)

where $S_L$, $S_{\theta}$ and $S_{n_{SiO_2}}$ are the standard deviations of the respective variables, and

$$ \frac{\partial A}{\partial L} = \mu $$

(17)
\[
\frac{\partial A}{\partial n_{SiO_2}} = \left( \frac{1}{n_{SiO_2}} - \frac{1}{n_{SiO_2} + 1} - \frac{1}{n_{SiO_2} + n_i} \right) \frac{4}{\ln 10}.
\]  

(18)

The full expression of \( \frac{\partial A}{\partial \theta} \) is a function of \( \sin \theta \), suggesting \( \lim_{\theta \to 0} \frac{\partial A}{\partial \theta} = 0 \), thus the error propagated from the small uncertainty of \( \theta \) is negligible. The substitution of Eqs. (S14-18) into Eq. (S13) derives SD of the extinction coefficient as:

\[
S_\mu = \frac{1}{L_2-L_1} \sqrt{6\mu^2 S_L^2 + \frac{64}{(\ln 10)^2} \left( \frac{1}{n_{SiO_2}} - \frac{1}{n_{SiO_2} + 1} - \frac{1}{n_{SiO_2} + n_i} \right)^2 S_n^2}.
\]  

(19)

The forefront variables concerned are not intended to be exhaustive. Other minor experimental uncertainties, e.g., from the temperature fluctuation, are not included. As suggested by Højerslev and Trabjerg \(^{20}\) and Röttgers \textit{et al.} \(^{21}\), the temperature-dependent offset is at the scale of \( 10^{-7} \text{ cm}^{-1} \text{°C}^{-1} \), which can be ignored compared with the uncertainties caused by the variables listed above.

\textit{S4.2 Experimental validation of the measurement limit}

\[\text{(a)}\]

\[\text{(b)}\]

\[\text{(c)}\]

\[\text{(d)}\]
Figure. S4 The repeated (× 4) extinction measurements of a H$_2$O-DMSO mixture (mass ratio 70:30) via “Four step measurement method”, equivalent to a total of 16 spectrophotometric scans through V-660 (a, 350-850 nm) and V-670 (b, 850-1400 nm) spectrophotometers. (c, d) The SD of the measured extinction coefficients in the mean of 16 spectrophotometric scans by the respective spectrophotometers, which shows the good agreement with the instrumental detection limit obtained in Section S1.5.

References

1. Litjens, R. A., Quickenden, T. I. & Freeman, C. G. Visible and near-ultraviolet absorption spectrum of liquid water. Applied optics 38, 1216-1223 (1999).
2. Dawson, L. & Hulburt, E. The absorption of ultraviolet and visible light by water. JOSA 24, 175-177 (1934).
3. Sullivan, S. A. Experimental study of the absorption in distilled water, artificial sea water, and heavy water in the visible region of the spectrum. JOSA 53, 962-968 (1963).
4. Boivin, L.-P., Davidson, W., Storey, R., Sinclair, D. & Earle, E. Determination of the attenuation coefficients of visible and ultraviolet radiation in heavy water. Applied optics 25, 877-882 (1986).
5. Otanicar, T. P., Phelan, P. E. & Golden, J. S. Optical properties of liquids for direct absorption solar thermal energy systems. Solar Energy 83, 969-977 (2009).
6. Kedenburg, S., Vieweg, M., Gissibl, T. & Giessen, H. Linear refractive index and absorption measurements of nonlinear optical liquids in the visible and near-infrared spectral region. Optical Materials Express 2, 1588-1611 (2012).
7. Li, X., Liu, L., Zhao, J. & Tan, J. Optical properties of sodium chloride solution within the spectral range from 300 to 2500 nm at room temperature. Applied spectroscopy 69, 635-640 (2015).
8. Wang, C., Tan, J. & Liu, L. Wavelength and concentration-dependent optical constants of NaCl, KCl, MgCl$_2$, CaCl$_2$, and Na 2 SO 4 multi-component mixed-salt solutions. Applied optics 56, 7662-7671 (2017).
9. Segelstein, D. J. The complex refractive index of water, University of Missouri–Kansas City, (1981).
10. Bachmann, S. J. & van Gunsteren, W. F. Polarizable model for DMSO and DMSO–water mixtures. The Journal of Physical Chemistry B 118, 10175-10186 (2014).
11. Petrova, T. & Dooley, R. Revised release on surface tension of ordinary water substance. Proceedings of the International Association for the Properties of Water and Steam, Moscow, Russia, 23-27 (2014).
12. Reisler, E. & Eisenberg, H. Refractive Indices and Piezo-optic Coefficients of Deuterium Oxide, Methanol, and Other Pure Liquids. The Journal of Chemical Physics 43, 3875-3880 (1965).
13. Cooper, J. & Dooley, R. IAPWS release on surface tension of heavy water substance. International Association for the Properties of Water and Steam (IAPWS), Charlotte, NC (1994).
14. Schrader, A. M. et al. Correlating steric hydration forces with water dynamics through surface force and diffusion NMR measurements in a lipid–DMSO–H$_2$O system. Proceedings of the National Academy of Sciences 112, 10708-10713 (2015).
15. http://www.chemspider.com/Chemical-Structure.67699.html.
16. Kratochvil, J., Kerker, M. & Oppenheimer, L. Light scattering by pure water. The Journal of Chemical Physics 43, 914-921 (1965).
17 Cohen, G. & Eisenberg, H. Light scattering of water, deuterium oxide, and other pure liquids. *The Journal of Chemical Physics* **43**, 3881-3887 (1965).

18 Haynes, L. L., Schmidt, R. L. & Clever, H. L. Thermodynamic properties of acetone, dimethyl sulfoxide, and their solutions by Rayleigh light scattering. *Journal of Chemical and Engineering Data* **15**, 534-536 (1970).

19 Katime, I., Cesteros, L. C. & Strazielle, C. Light scattering from binary mixtures of 1, 2-dichloroethane, acetonitrile, dimethylformamide and ethyl acetate. Excess gibbs functions. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **80**, 1215-1224 (1984).

20 Trabjerg, I. & Højerslev, N. K. Temperature influence on light absorption by fresh water and seawater in the visible and near-infrared spectrum. *Applied optics* **35**, 2653-2658 (1996).

21 Röttgers, R., McKee, D. & Utschig, C. Temperature and salinity correction coefficients for light absorption by water in the visible to infrared spectral region. *Optics express* **22**, 25093-25108 (2014).