Measurement of Solvation Ability of Solvents by Porphyrin-Based Solvation/Desolvation Indicators

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ABSTRACT: A new solvent scale, solvation ability (SA), was developed to arrange solvents in the order of their SA for large π-conjugated compounds. The SA of a solvent was determined in a binary solvent system of an assessed solvent and a standard “good” solvent (GS) or “poor” solvent (PS), chloroform or methylcyclohexane, respectively, in the presence of two types of solvation/desolvation indicators, 1Zn2 and 2Zn2. The latter comprises bis(imidazolylporphyrinatozinc) linked via a 1,3-butadiynylene moiety having linear alkyl and hydrophilic side chains, respectively. GSs and PSs give extended (E-) and stacked (S-) supramolecular polymers of the indicators, respectively. SA values are defined as vol % of the standard solvent added to an assessed solvent to give the balance point where comparable amounts of E- and S-polymers of the indicators coexist. GSs and PSs have positive and negative signs, respectively. In this study, the SA of 25 solvents was determined. The SA values with indicator 1Zn2 were as follows: ethyl acetate (−81), hexane (−66), toluene (−50), cyclohexane (−47), CCl4 (−25), chloroform (50), and nitrobenzene (79).

1. INTRODUCTION

The terms “solvent effect” and “solvation dependence” appear frequently in the scientific literature. Most solvent effects and solvent-dependent phenomena in chemical reactions involve the solvation of starting materials and products, as well as the intermediates and the transition states, resulting in changes in the energy landscapes, which in turn control the equilibrium ratios, product yields, and reaction rates. Solvation of solvents to the materials is sometimes realized, and solvent-dependent phenomena have been explained by the physical properties of solvents, such as the dielectric constant (ε), refractive index (n), cohesive energy density (CED), and an empirical solvent index, such as π* and EΠ(30)2 derived using solvatochromic compounds. In electron and charge transfer systems, for example, polar solvents that have higher dielectric constants can stabilize the charged materials. Solvation of ions and polar compounds is also favored in polar solvents for the same reason. In the majority of these cases, relatively strong charge−dipole, dipole−dipole, and hydrogen bonding interactions are the dominant contributors. In contrast, weak interactions, such as arene−arene, arene−perfluoroarene,4 sulfur−arene, cation−π5,6 and anion−π7,8 interactions, involving neutral and nonpolar or less-polar arenes and π-conjugated compounds, are also important in biological molecules, as well as in synthetic molecules and supramolecules.8−12 The weak interactions are affected by the solvent and peripheral substituents.11−25 However, solvation of neutral and nonpolar or less-polar arenes and the role of peripheral substituents on the arenes remain unclear. This is because weak interactions among solvent molecules, arenes, and peripheral substituents are related, as in a many-body problem, but they are obscured by other strong interactions.

Thus, no existing method can measure the solvation ability (SA)/desolvation ability of solvents toward neutral and nonpolar or less-polar arenes separately from the other strong interactions.

Arene−arene interaction, so-called π−π interaction, is one of the most important nonbonding interactions in supramolecular polymerization.11,22−26 Understanding the solvent dependence and substituent effect of the π−π interaction is an important issue in science. Therefore, creating a solvent scale for the π−π interaction among neutral and nonpolar arenes is considered to be useful for carrying out detailed studies of solvent dependencies on π−π interactions.

One of the methods used to prepare such a solvent scale is measuring the abundance ratio between two solvent-dependent conformational isomers in various solvents20,27−30 in which π−π interactions are associated to form one of the isomers. Another method is obtaining association constants of self-assembled dimer and polymer systems through π−π
interactions in various solvents. From the association constant, the solvent-dependent Gibbs free energy difference (ΔG) between the monomer and the dimer (polymer) is determined.11,16,17,21,22,31

Although solvent-dependent ΔG values have been reported for several dynamic systems, they are considered inadequate in terms of the numbers and types of solvents assessed to study solvent dependencies on π−π interactions systematically. Here, we report a new method for measuring the SA of solvents by using the solvation/desolvation indicators 1Zn2 and 2Zn2 (Figure 1) that we developed previously.32,33

2. RESULTS AND DISCUSSION

The indicators comprise bisimidazolylporphyrinatozinc linked via a 1,3-butadiynylene moiety. They form extended (E-) or stacked (S-) polymers exclusively through two types of complementary coordination bonds and π−π interactions among the porphyrin units inside the S-polymer (Figure 2). The two types of coordination bonds are only weakly solvent-dependent, whereas the π−π interactions are highly solvent-dependent. Therefore, the solvent dependency of the formation of E- or S-polymers can be applied to the creation of a solvent scale for the π−π interaction. In this system, any type of liquid/solvent (except for very strongly coordinating to the zinc porphyrin moieties, such as pyridine) can be used with a small amount of the indicator. Hence, many solvents/liquids of various types can be indexed.

In our system, it is difficult to determine the energy differences between E- and S-polymers in only one solvent as in most cases, only E- or S-polymers are observed. Instead, a balance point could be created by adding a GS to a PS or by adding a PS to a GS in which E- and S-polymers exist in comparable amounts.

We noticed that the relative SA of solvents could be determined by comparing the ease with which the balance points could be prepared. The method appears to resemble an acid/base titration using phenolphthalein as an indicator. Interconversion between E- and S-polymers is illustrated in Figure 3. Because E- and S-polymers are formed exclusively in most solvents, the balance point exists only under limited binary solvent conditions. Upon titration, the balance point can be detected as a steep inflection point.

Titration is very convenient for creating the balance point. However, the final concentration of the balance point may vary depending on the solvent used. To compare the SA of various solvents, the conditions (e.g., concentration and temperature) must be held constant. We elected to use the tournament style to measure the SA (Figure 4). In the experiments, the concentration and temperature were regulated to 2.5 × 10^-6 M and 298 K, respectively.

Various ratios of binary mixtures were prepared. The indicators were dissolved therein to give the same concentrations. As standard GSs and PSs, CHCl₃ and methylcyclohexane (MCH) were selected, respectively. These are well miscible with other solvents. To assess PSs, CHCl₃ was used, whereas methylcyclohexane was used to assess GSs. Typical UV-vis spectral results are shown in Figure 5.

Here, CH₃CN was assessed as a PS. The flow of the assessment followed the tournament style (Figure 4). First, when a 50:50 v/v mixture of CH₃CN and CHCl₃ was used (Figure 5a), only S-polymer was observed as a characteristic peak at 768 nm. Second, when a 25:75 mixture was used (Figure 5b), a trace amount of E-polymer was observed as a...
shoulder signal at 740 nm. Third, when a 13:87 mixture was used (Figure 5e), only E-polymer was observed. Then, when an 18:82 mixture was used (Figure 5d), only E-polymer was observed. Finally, the balance point was determined to be 21:79 (Figure 5c) where almost equal amounts of E- and S-polymers coexisted. It is noteworthy that the balance point exists only in a narrow range of the binary mixtures. This is because the formations of E- and S-polymers are exclusive to each other. The inflection point between E- and S-polymers is very steep and an accurate balance point was reached at 21:79 ± 3%. Similar steep changes were observed in all other solvents assessed.

To combine the scales of solvation and desolvation, SA is defined as follows. If CHCl₃ is used as a GS to assess a PS, then the sign of the SA of the assessed solvent is negative. In contrast, if MCH is used as a PS to assess a GS, then the sign is positive. The absolute values of the SA correspond to the vol % of the added standard solvents. We can compare the SA values with ±5% accuracy, except for p-xylene (±7%). In this study, 25 solvents were assessed. All their UV–vis spectra are shown in Figures S1–S5. In Figure 6, the SA values for 1Zn₂ are represented as bar graphs. The error bars indicate the accuracy of the SA values.

The solvents were classified into five groups: (a) polar nonaromatic compounds, (b) nonpolar and nonaromatic compounds (alkanes), (c) benzene and methylated benzenes, (d) chloro-organic compounds, (e) and functionalized benzene. AcOEt: ethyl acetate; MeCN: acetonitrile; AcOBu: n-butyl acetate; DME: 1,2-dimethoxyethane; THF: tetrahydrofuran. Standard GS: CHCl₃; standard PS: MCH.

Figure 4. Tournament style used to determine the balance points in various solvents using solvation/desolvation indicators 1Zn₂ and 2Zn₂.

Figure 5. UV–vis spectra of 1Zn₂ in various binary mixtures of MeCN and CHCl₃ (2.5 × 10⁻⁶ M, 298 K). MeCN:CHCl₃ = (a) 50:50, (b) 25:75, (c) 21:79, (d) 18:82, and (e) 13:87. Characteristic peaks of S- and E-polymers are observed at 768 and 740 nm, respectively. The balance point coexisting in the S- and E-diomers is (c) 21:79.

Figure 6. Solvation ability of 25 solvents for 1Zn₂ (2.5 × 10⁻⁶ M, 298 K). (a) Polar nonaromatic compounds, (b) nonpolar and non-aromatic compounds (alkanes), (c) benzene and methylated benzenes, (d) chloro-organic compounds, (e) and functionalized benzene. AcOEt: ethyl acetate; MeCN: acetonitrile; AcOBu: n-butyl acetate; DME: 1,2-dimethoxyethane; THF: tetrahydrofuran. Standard GS: CHCl₃; standard PS: MCH.
In group (c) solvents, although the substituent effect was observed, no trend was observed in the direction and degree of the difference between 1-Zn and 2-Zn.

Table S1 lists all SA values of the 25 solvents obtained experimentally in this work, together with their CEDs, empirical solvent scales (π* and ET(30)), refractive indexes (n), and dielectric constants (ε). In Figures S6–S10, relationships between SA values and CED, π*, ET(30), n, and ε are plotted, respectively. Overall, there was little relationship observed between the SA values and the empirical solvation scales and physical properties of solvents assessed, especially for group (a) solvents.

Wüthner and co-workers,16 Müllen and co-workers,17 and Moore and co-workers11 have reported polymerization constants of perylene bisimide derivatives 1–3,16 hexabenzocoronene derivatives 4 and 5,17 and phenylene ethynylene macrocycle derivative 6,11 respectively, in three to eight different solvents. Here, all the polymers are assumed to be self-assembled by isodesmic models. The relationships between their reported polymerization energies and the SA values obtained in this study are plotted in Figures 8–10 and Figures S11–S13 (data tabulated in Tables 1–3 and Tables S2–S4). Although only a few solvents were used, relatively good correlations were obtained. Thus, a solvent having a larger negative SA tends to give a larger negative ΔG of polymer formation. These results suggest that the SA values obtained in this work offer one of the solvent scales to estimate π–π interaction between large π-conjugated compounds.

3. CONCLUSIONS

We successfully constructed a new solvent scale, SA, using the solvation/desolvation indicators 1-Zn and 2-Zn. SA values are defined as vol % of a standard solvent added to an assessed solvent to give the balance point where comparable amounts of

![Figure 7](image1.png)

Figure 7. Solvation ability of 19 solvents (having a negative sign) for 1-Zn and 2-Zn (2.5 × 10^-6 M, 298 K): (a) polar nonaromatic compounds, (b) nonpolar, nonaromatic compounds, and (c) benzene and methylated benzenes. Standard GS: CHCl3; standard PS: MCH.

![Figure 8](image2.png)

Figure 8. Relationships between SA and ΔG° for formation of oligomer of perylene bisimide 1.

![Figure 9](image3.png)

Figure 9. Relationships between SA and ΔG° for formation of oligomer of hexabenzocoronene 5.

![Figure 10](image4.png)

Figure 10. Relationships between SA and ΔG° for formation of oligomer of phenylene ethynylene macrocycle 6.

| solvent                  | ΔG° / kJ mol⁻¹ | 1-Zn  | 2-Zn  |
|--------------------------|---------------|-------|-------|
| MCH                      | −40.9         | −50   | −57   |
| dibutyl ether            | −36.9         | −69   | −66   |
| diethyl ether            | −37.3         | −74   | −70   |
| CCl₄                     | −30.0         | −25   | −29   |
| toluene                  | −26.5         | −50   | −44   |
| THF                      | −27.0         | 44    | 7     |
| CH₂Cl₂                   | −18.3         | 57    | 44    |
| CHCl₃                    | −13.8         | 50    | 44    |

Table 1. Relationships between SA and ΔG° for Formation of Oligomer of Perylene Bisimide 1

| solvent                  | ΔG° / kJ mol⁻¹ | 1-Zn  | 2-Zn  |
|--------------------------|---------------|-------|-------|
| 1,1,2,2-tetrachloroethane| −17.1         | 76    | 58    |
| THF                      | −21.7         | 44    | 7     |
| benzene                  | −24.2         | −47   | −25   |

Table 2. Relationships between SA and ΔG° for Formation of Oligomer of Hexabenzocoronene 5
Table 3. Relationships between SA and ΔG° for Formation of Oligomer of Phenylene Ethynylene Macrocyle 6

| solvent | ΔG° / kJ mol⁻¹ | solvation ability (SA) |
|---------|----------------|------------------------|
| CHCl₃   | -9.69          | 1Zn₂                   |
| THF     | -14.5          | 2Zn₂                   |
| benzene | -17.6          | 44                     |
| acetone | -23.8          | 7                       |

E- and S-polymers of the indicators coexist. As the SA values for samples were collected at the same concentrations and temperatures, the values can be directly compared. Although there was little correlation between SA values and the empirical solvent scales (reported previously) and physical solvent properties, SA and polymerization constants of large π-conjugated compounds seemed to be correlated. As the method is applicable to any solvent/liquid material, extensive data on SA values can be collected. Such data will be useful for studying the solvation and desolvation of large π-conjugated compounds.

4. EXPERIMENTAL SECTION

4.1. General Procedure. All chemicals and solvents were of commercial reagent quality and used without further purification unless otherwise stated. CHCl₃ (Kanto, extra pure) stabilized with 0.5–1% ethanol was used. UV–vis absorption spectra were collected on a JASCO V-660 spectrometer at 298 K.

4.2. UV–Vis Titration. An aliquot (30 μL) of a 2.5 × 10⁻⁴ M chloroform solution of 1Zn₂ or 2Zn₂ was added to 3 mL of mixtures of chloroform and “poor” solvents to be assessed or MCH and “good” solvents to be assessed. The UV–vis spectra were recorded as shown in Figures S1–S5.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04461.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.S. acknowledges the significant support from Tokyo University of Science (TUS).

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ACS Omega 2020, 5, 6045–6050
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