Prediction of Solvatochromic Polarity Parameters for Aqueous Mixed-Solvent Systems

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Abstract: Solvent polarity is important data being used in solvent selections for preliminary engineering design of chemical processes. In this work, a predictive model is proposed for estimating the solvatochromic polarity of electronic transition energy ($E_T$) of Reichardt indicator for aqueous mixtures. To validate the model, the $E_T$ values of eighteen aqueous mixtures collected from the literature were used. The predictive model provided a good estimation of $E_T$ values with an overall deviation of 2.1%, compared with an ideal model (5.1%) from the mole fraction average. The linear relationship of the contribution factor of hydrogen bond donor interactions ($CF_{HBD}$) in the predictive model with Kamlet–Taft acidity was newly proposed in order to extend the model for other aqueous mixtures. The predictive model is applicable to many aqueous mixtures and simply requires three properties of pure components as: (i) $E_T$ values, (ii) gas-phase dipole moment and (iii) Kamlet–Taft acidity.

Keywords: solvation; merocyanine; solvent selection; green solvents; solvent polarity

1. Introduction

The use of aqueous mixtures is preferable in many chemical processes (e.g., biomass conversion [1,2], separation and fractionation [3] and processing of active pharmaceutical ingredients [4–6]) because of the benefit of a safe solvent. Solvent polarity is an informative data being used in solvent selections [7–10] for preliminary engineering design and understanding the solvent effects on the chemical processes [11]. Polarity [12] is generally referred to as a solvent’s capability for solute dissolution and can be quantified with many physical properties of solvents (e.g., electronic transition energy, solubility parameters and dielectric constant). Among the physical properties of solvents, the electronic transition energy ($E_T$) is commonly used to quantify an empirical solvent scale (also known as Reichardt’s polarity) because the parameter requires a simple measurement using a solvatochromic technique with an indicator [13,14].

The $E_T$ values of aqueous mixtures [15] generally tend to have a negative deviation from the ideality line (Figure 1b) due to preferential interactions of an indicator with cosolvents. There are the correlative models (preferential solvation model [16–18] and Jouyban–Acree model [19]) for representing a preferential trend in the aqueous mixtures, while there is no predictive model for estimating $E_T$ values of the mixture. It is supposed that an ideal model (Equation (1), Section 2.1) is most likely applied for estimations due to a simple calculation from a mole fraction average. However, the ideal model (dashed line, Figure 1b) caused a large deviation from experimental data (symbol, Figure 1b).
According to our previous works, the predictive models for estimating $E_T$ values [20] and Kamlet-Taft dipolarity/polarizability (KT-$\pi^*$) [21,22] of nonpolar-polar mixtures have been proposed and the models provided a good predictive result as shown by the example for $E_T$ values in Figure 1a (blue solid line). Since both nonpolar-polar mixtures (Figure 1a) and aqueous mixtures (Figure 1b) show a similar negative deviation from ideality, the predictive model (Equation (2)) is expected to be applicable to the aqueous mixtures.

With preliminary assessment, the predictive model (Equation (2)) is applicable to the aqueous mixtures (blue solid line, Figure 1b). The objective of this work is to predict the polarity parameters ($E_T$ values) of aqueous systems using the predictive model (Equation (2)). The predictive model was validated by experimental $E_T$ data of Reichardt indicator for eighteen aqueous mixtures that were collected from the literature [15,23–25].

![Figure 1. Comparison in electronic transition ($E_T$, kcal·mol$^{-1}$) for (a) nonpolar-polar systems of carbon tetrachloride (1)—dimethylformamide (2) and (b) aqueous systems of water (1)—dimethylformamide (2) as a function of mole composition of component 2 ($x_2$) at 25 °C. Black dashed lines show calculations from the ideal model (Equation (1)). Blue solid lines show predictions with the predictive model (Equation (2)) without considering hydrogen bond donor (HBD) contribution factor ($CF_{HBD} = 1$). The $E_T$ values in part (a) were collected from the phenol blue indicator [26]. The $E_T$ values in part (b) were obtained from the Reichardt indicator [15].](image)

2. Models and Methods

2.1. Ideal Model

The ideal model is used to compare the deviation of experimental data from ideality and is defined by Equation (1):

$$E_T^{\text{ideal}} = x_1E_{T,1}^0 + x_2E_{T,2}^0$$  \hspace{1cm} (1)

where $E_{T,i}^0$ is the electronic transition energy of pure component $i$. Component 1 denotes water and component 2 denotes hydrogen bond acceptor (HBA) cosolvent or hydrogen bond donor (HBD) cosolvent.
2.2. Predictive Model

A predictive model was originally proposed for estimating Kamlet–Taft dipolarity/polarizability (KT-π*) [22] of binary nonpolar-polar mixtures with an assumption that the gas-phase dipole moment (μ) of the polar component can quantify a trend of mixture KT-π* values at a fixed mole composition. Due to a linear relationship between KT-π* and $E_T$ values (homomorphism line, Figure 2), the predictive model for KT-π* values can directly transform into a function form for estimating $E_T$ values for nonpolar-polar mixtures reported in our previous work [20], as shown by Equation (2). In this work, the model (Equation (2)) was used to predict the $E_T$ values of aqueous mixtures due to similar negative deviation trends in both aqueous mixtures and nonpolar-polar mixtures as mentioned in the introduction (Figure 1).

$$\Delta E_{T,\text{mix}}^N = \mu_2(1.981x_1 + 0.181x_2) \times CF_{\text{HBD}}$$

where $\mu_2$ is the gas-phase dipole moment of component 2. The 1.981 and 0.181 values are the universal Wilson constant parameters ($\Lambda_{12}$ and $\Lambda_{21}$) for predictions and were evaluated by correlating experimental data with Wilson thermodynamic excess function [22].

The $\Delta E_{T,\text{mix}}^N$ is relative normalized electronic transition energy and defined by Equations (3)–(5).

$$\Delta E_{T,\text{mix}}^N = E_{T,\text{mix}}^N - (x_1E_{T,1}^N + x_2E_{T,2}^N) = E_{T,\text{mix}}^N - x_2$$

$$E_{T,\text{mix}}^N = \frac{E_{T,\text{mix}}^0 - E_{T,1}^0}{E_{T,2}^0 - E_{T,1}^0}$$

$$E_T (\text{kcal} \cdot \text{mol}^{-1}) = \frac{28591}{\lambda_{\text{max}} (\text{nm})}$$

where $\lambda_{\text{max}}$ (nm) is the maximum absorption of the wavelength of a solvatochromic indicator (Reichardt indicator) obtained from UV-Vis spectroscopy. The $E_{T,\text{mix}}^N$ and $E_{T,\text{mix}}^0$ are the electronic transition energy and the normalized electronic transition energy of the binary mixtures. To apply the predictive model (Equation (2)) to aqueous systems studied in this work, component 1 refers to water and component 2 refers to cosolvent (HBA or HBD). According to normalization (Equation (4)), the $E_{T,1}^N$ and $E_{T,2}^N$ of pure components 1 and 2 in Equation (3) are set equal to zero and unity, respectively.

The $CF_{\text{HBD}}$ parameter in Equation (2) is the HBD contribution factor and the parameter is only applied to an aqueous mixture of HBD cosolvents due to specific interaction of HBD solvent with indicator [20] that causes a deviation in the pure $E_{T,2}^0$ value (HBD solvent) from the homomorphism line (Figure 2). The $CF_{\text{HBD}}$ values in Equation (6) can be estimated by a deviation of the actual $E_T$ value of pure HBD cosolvent ($E_{T,2}^0$) from the homomorphism line in Figure 2 as shown in Equation (6).

$$CF_{\text{HBD}} = E_{T}^{0,\text{Non}} - E_{T,2}^0$$

where $E_{T}^{0,\text{Non}}$ is a non-HBD bonding $E_T$ value of pure HBD cosolvents defined as a linear function of dipolarity/polarizability (KT-π*), that is the homomorphism linear line in Figure 2. The linear relationships of $E_{T}^{0,\text{Non}}$ were given in detail in our previous work [20], and the $CF_{\text{HBD}}$ values of nine HBD cosolvents studied in this work are given in Table 1 along with their Kamlet-Taft acidity ($\alpha$).

An average $CF_{\text{HBD}}$ value from three indicators (Table 1) was used in predictions (Equation (2)) for nine aqueous mixtures of HBD cosolvents. To extend to other HBD cosolvents, a linear relationship of $CF_{\text{HBD}}$ with Kamlet-Taft acidity ($\alpha$) was proposed in Equation (7) and Figure 3, because the $\alpha$ values of HBD cosolvents are widely available in the literature [27,28].

$$CF_{\text{HBD}} = 2.766\alpha - 0.0115, \quad (R^2 = 0.89)$$
Figure 2. Plot of Kamlet–Taft dipolarity/polarizability (KT-π*) and electronic transition (E_T, kcal·mol^{-1}) of three indicators as (a) Reichardt indicator, (b) phenol blue indicator and (c) Nile red indicator in (▲) pure nonpolar solvent, (●) pure hydrogen bond acceptor (HBA) solvent and pure polar hydrogen bond donor (HBD) solvent. Symbols of HBD solvents are given in Table 1. Solid line shows a linear relationship (reference homomorphism line) of KT-π* values and E_T values of pure nonpolar solvents and pure HBA solvents. The deviation of E_T values of pure HBD solvents from the linear line is due to HBD contribution. Data are given in detail in our previous work [20].
Table 1. Pure properties of hydrogen bond donor (HBD) at 25 °C showing Kamlet-Taft acidity (KT-α) [27,28] and HBD contribution factor (CF_{HBD}) evaluated from three indicators (Ind.) a.

| Entry | HBD Solvents | KT-α | Actual CF_{HBD} (-) b | Calculated CF_{HBD} (-) c |
|-------|---------------|------|-----------------------|---------------------------|
|       | (Symbol)      | (Abbreviation) | (-) | Ind. 1 | Ind. 2 | Ind. 3 | Avg | (Equation (7)) |
| 1     | (X)           | Methanol (MeOH) | 1.00 | 3.65 | 2.32 | 2.34 | 2.77 | 2.75 |
| 2     | (X)           | Ethanol (EtOH)  | 0.89 | 3.05 | 2.21 | 2.21 | 2.49 | 2.45 |
| 3     | (X)           | 1-Propanol (PrOH) | 0.84 | 2.79 | 1.96 | 2.51 | 2.42 | 2.31 |
| 4     | (X)           | 2-Propanol (iPrOH) | 0.76 | 2.44 | 1.72 | 2.17 | 2.11 | 2.09 |
| 5     | (X)           | 1-Butanol (BuOH) | 0.84 | 2.65 | 2.04 | 3.04 | 2.58 | 2.31 |
| 6     | (X)           | Tert-Butanol (T-BuOH) | - | 2.65 | - | - | 2.65 | - |
| 7     | (X)           | Ethylene glycol (ETG) | 0.90 | 3.01 | - | 1.59 | 2.30 | 2.48 |
| 8     | (X)           | Acetic acid (AcOH) | 1.12 | 4.34 | 1.83 | 2.78 | 2.98 | 3.09 |
| 9     | (X)           | Formamide (FA)   | 0.63 | 2.09 | 1.27 | 1.32 | 1.56 | 1.73 |

a Indicators: Ind. 1 = 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino) phenolate indicator; Ind. 2 = phenol blue and Ind. 3 = Nile red. b Actual CF_{HBD} values are evaluated from Figure 2. c Calculated CF_{HBD} values are obtained from Equation (7).

Figure 3. Relationship of HBD contribution factor (CF_{HBD}) with Kamlet-Taft acidity (KT-α) of hydrogen bond donor (HBD) cosolvents at 25 °C. The CF_{HBD} and KT-α data are given in Table 1. Dashed line represents Equation (7). Symbols of HBD solvents are given in Table 1.

Figure 4 shows a flow chart developed in this work for predicting $E_T$ values of aqueous mixtures that is divided into five steps. In step 1, pure properties of electronic transition energy ($E_T^0$) and gas-phase dipole moment ($\mu_2$) of components 1 and 2 are compiled from the literature. In step 2, solvent characteristics of component 2 (cosolvent) are determined to check HBD ability by considering their molecular structures and KT-acidity. For example, HBD cosolvents are able to donate a proton so that their KT-acidity values are relatively high (Table 1). On the other hand, HBA cosolvents lack proton donor groups, and thus, the CF_{HBD} value of HBA cosolvent is equal to unity. In step 3, CF_{HBD} values of HBD cosolvent are calculated by either Figure 2 or Equation (7). In steps 4 and 5, the predictive model (Equation (2)) was used to estimate the $E_T$ values of aqueous mixtures and was validated, respectively. To validate the predictive model in step 5, nine aqueous mixtures of HBA cosolvents and nine aqueous mixtures of HBD cosolvents (Table 2) were used and discussed in
Section 3. Table 2 tabulates the $E^0_{T,i}$, $\mu_2$ [29], Hunter basicity ($\beta^H$) of component 2 [30,31] and $CF^{HBD}$ values of solvents used in the predictions.

### Table 2. Comparison between electronic transition ($E_T$, kcal·mol$^{-1}$) values calculated with the predictive model (Equation (2)) and ideal model (Equation (1)) for nine aqueous mixtures of hydrogen bond acceptor (HBA) cosolvents and nine aqueous mixtures of hydrogen bond donor (HBD) cosolvents at 25 °C that were obtained with Reichardt indicator. Average relative deviations (ARD) were calculated with Equation (8) along with dipole moment of component 2 ($\mu_2$), HBD contribution factor ($CF^{HBD}$), Hunter basicity ($\beta^H$) of component 2, pure properties of electronic transition energy ($E^0_{T,i}$) and the number of data used (N). Gray-shaded rows indicate the ARD results estimated from the calculated $CF^{HBD}$ (Equation (7)).

| Entry | Component 2 | $\mu_2$ | $CF^{HBD}$ | $\beta^H$ | $E^0_{T,i}$ | ARD (%) | N | Ref. |
|-------|-------------|---------|------------|-----------|-------------|---------|---|-----|
|       | (Symbol)    | D       | (+)        | (-)       | (1)         | (2)     |   |     |
| 1     | ACN         | 3.92    | 1.00       | 4.7       | 63.10       | 46.00   | 6.64 | 3.36 | 11  | [15] |
| 2     | THF         | 1.63    | 1.00       | 5.3       | 63.10       | 37.50   | 4.36 | 4.97 | 11  | [15] |
| 3     | GBL         | 3.82    | 1.00       | 5.3       | 63.00       | 44.62   | 3.45 | 4.42 | 12  | [23] |
| 4     | GVL         | 5.30    | 1.00       | 5.3       | 63.00       | 47.85   | 2.61 | 6.27 | 12  | [23] |
| 5     | PYR         | 3.10    | 1.00       | 8.3       | 63.00       | 47.90   | 1.49 | 5.24 | 11  | [24] |
| 6     | NMP         | 4.09    | 1.00       | 8.3       | 63.00       | 42.20   | 1.85 | 9.85 | 10  | [24] |
| 7     | DMF         | 3.86    | 1.00       | 8.3       | 63.10       | 43.80   | 1.37 | 4.77 | 11  | [15] |
| 8     | DMSO        | 3.96    | 1.00       | 8.9       | 63.10       | 45.00   | 0.75 | 5.29 | 11  | [15] |
| 9     | Pyridine    | 2.19    | 1.00       | 7.0       | 63.10       | 40.30   | 1.29 | 4.77 | 11  | [15] |
|       | Overall (aqueous HBA mixtures) | | | | | 2.65 | 5.44 |  |  |
### Table 2. Cont.

| Entry | Component 2 | $\mu_2$ | $C_{f,HBD}$ | $\beta^H$ | $E^H_T$ | ARD (%) | N | Ref. |
|-------|-------------|---------|-------------|-----------|----------|---------|----|------|
| (Symbol) | (D) | (-) | (-) | (1) | (2) | Predict | Ideal |
| 10 (⊥) | Water (1)–HBD cosolvent (2) | MeOH | 1.70 | 2.77 | 5.8 | 63.10 | 55.70 | 0.23 | 2.40 | 11 | [15] |
| | | | | | | | | 2.25 | 
| 11 (⊥) | | EtOH | 1.69 | 2.49 | 5.8 | 63.10 | 51.70 | 0.34 | 3.92 | 11 | [15] |
| | | | | | | | | 2.45 | 
| 12 (⊥) | | PrOH | 1.66 | 2.42 | 5.8 | 63.10 | 50.60 | 1.42 | 5.14 | 11 | [15] |
| | | | | | | | | 2.31 | 
| 13 (⊥) | | iPrOH | 1.66 | 2.11 | 5.8 | 63.10 | 48.70 | 2.64 | 6.73 | 11 | [15] |
| | | | | | | | | 2.09 | 
| 14 (⊥) | | BuOH | 1.66 | 2.58 | 5.8 | 63.10 | 43.90 | 2.58 | 4.28 | 10 | [15] |
| | | | | | | | | 2.31 | 
| 15 (⊥) | | T-BuOH | 1.67 | 2.65 | 5.8 | 63.10 | 43.30 | 4.67 | 12.54 | 11 | [25] |
| | | | | | | | | 2.48 | 
| 16 (⊥) | | ETG | 2.31 | 2.30 | - | 63.10 | 56.24 | 0.50 | 2.44 | 10 | [15] |
| | | | | | | | | 2.48 | 
| 17 (⊥) | | AcOH | 1.74 | 2.98 | 5.3 | 63.10 | 55.00 | 1.03 | 2.10 | 11 | [15] |
| | | | | | | | | 3.09 | 
| 18 (⊥) | | FA | 3.73 | 1.56 | 5.8 | 63.10 | 53.74 | 0.97 | 3.22 | 11 | [15] |
| | | | | | | | | 1.73 | 
| Overall (both HBA and HBD mixtures) | | | | | | | | 1.60 | 4.75 | |

The $\mu_2$ values for all solvents are taken from handbook [29], except for GVL [32]. The overall average relative deviation (ARD) values are calculated without considering the values in the gray-shaded rows. Solvent abbreviations for HBD cosolvent are given in Table 1. Solvent abbreviations for HBA cosolvent: ACN = acetonitrile; THF = tetrahydrofuran; GBL = gamma butyrolactone; GVL = gamma valerolactone; PYR = 2-pyrrolidinone; NMP = N-methyl-2-pyrrolidone; DMF = dimethylformamide and DMSO = dimethyl sulfoxide.

2.3. Evaluation of the Frameworks

Average relative deviation (ARD) was used to evaluate a deviation between experimental ($E^H_T^{Exp}$) and calculated ($E^H_T^{Cal}$) data as shown in Equation (8):

$$\text{ARD (\%)} = \frac{1}{N} \sum \left| \frac{E^H_T^{Cal} - E^H_T^{Exp}}{E^H_T^{Exp}} \right| \times 100$$

(8)

3. Results and Discussion

3.1. Prediction for Aqueous Mixtures of HBA Cosolvents

Figure 5 shows the $E_T$ values of nine aqueous mixtures of water (1)–HBA cosolvent (2) as a function of component 2 (HBA cosolvent). The $E_T$ values of all aqueous mixtures (Figure 5) exhibited a negative deviation from the ideality (dashed lines, Figure 5), except for the aqueous mixtures of acetonitrile (ACN), tetrahydrofuran (THF) and gamma-butyrolactone (GBL) that showed a sigmoid function (Figure 5a–c). Blue solid lines (Figure 5) show predicted $E_T$ values of the aqueous mixture using Equation (2) without $C_{f,HBD}$ value ($C_{f,HBD} = 1$) that generally tended toward the experimental data (symbols, Figure 5).

Table 2 shows a comparison of ARD values obtained between the ideal model (Equation (1)) and predictive model (Equation (2)) for the aqueous mixtures of HBA cosolvents (entries 1–9, Table 2) and HBD cosolvent (entries 10–18, Table 2). The predictive model (Equation (2)) generally provided a lower ARD value (2.7%, entries 1–9, Table 2) than that estimated from the ideal model (5.4%). However, the model gave a relatively high ARD value (entries 1–3, Table 2) for the aqueous mixtures that showed the sigmoid functions (Figure 5a–c). These results inferred a limitation of the predictive model and
were discussed later in Section 3.4. The predictive results of aqueous mixtures of HBD cosolvents were discussed in the following section.

**Figure 5.** Electronic transition of ($E_T$ (30), kcal·mol$^{-1}$) of nine aqueous mixtures of water (1)—hydrogen bond acceptor (HBA, 2) as a function of mole composition of component 2 ($x_2$) at 25 °C. Symbols (a–i) and reference sources are given in Table 2 (entries 1–9). Black dashed lines show calculations from the ideal model (Equation (1)). Blue solid lines show predictions with the predictive model (Equation (2)) without considering HBD contribution factor ($CF_{HBD} = 1$).

### 3.2. Prediction for Aqueous Mixtures of HBD Cosolvents

Figure 6 shows the $E_T$ values of nine aqueous mixtures of water (1)—HBD solvent (2) as a function of component 2 (HBD solvent) that also exhibited a negative deviation from the ideality. A comparison in predictive model (Equation (2)) with considering $CF_{HBD}$ value (Table 1) and without considering $CF_{HBD}$ value ($CF_{HBD} = 1$). Red solid lines in Figure 6 show predictions with considering $CF_{HBD}$ value, while the blue ones are the predictions without considering $CF_{HBD}$ value.

The predictive model with the addition of $CF_{HBD}$ values (red solid lines, Figure 6) could provide a better result in the calculated $E_T$ value that followed the experimental data than the result without the $CF_{HBD}$ value (blue solid lines, Figure 6). The ARD values obtained from the predictive model (Equation (2)) with considering $CF_{HBD}$ value (1.6%, entries 10–18, Table 2) are lower than those estimated from the ideal model (4.8%). Figure 7 shows parity plots of calculated $E_T$ values that are estimated from the predictive model (Figure 7a) and the ideal model (Figure 7b). The estimated $E_T$ values from the predictive model ($R^2 = 0.91$, Figure 7a) are less scattered than those obtained from the ideal model ($R^2 = 0.81$, Figure 7b).
Figure 6. Electronic transition of ($E_T$ (30), kcal·mol$^{-1}$) of nine aqueous mixtures of water (1)—hydrogen bond donor (HBD, 2) as a function of mole composition of component 2 ($x_2$) at 25 °C. Symbols (a–i) and reference sources are given in Table 2 (entries 10–18). Black dashed lines show calculations from the ideal model (Equation (1)). Blue solid lines show predictions with the predictive model (Equation (2)) without considering HBD contribution factor ($CF^{HBD} = 1$). Red solid lines show prediction with the predictive model (Equation (2)) with considering actual $CF^{HBD}$ values in Table 1. Green solid lines show prediction with the predictive model (Equation (2)) with considering calculated $CF^{HBD}$ values using Equation (7).

Figure 7. Parity plots of electronic transition ($E_T$) in eighteen aqueous mixtures obtained from (a) the predictive model (Equation (2), $R^2 = 0.91$) and (b) the ideal model (Equation (1), $R^2 = 0.81$). Symbols and conditions are defined in Table 2.
3.3. Evaluation of $C_f^{HBD}$ Methods for Predictions

In Section 3.2, the predicted $E_T$ values of aqueous mixtures of HBD cosolvents were estimated based on the actual $C_f^{HBD}$ values evaluated from Figure 2 and Table 1. In the section, a comparison in evaluated $E_T$ values between actual data (Table 1) and calculations with KT-acidity (Equation (7)) was made for predictions. Red solid lines (Figure 6) show predicted $E_T$ values of the mixtures with actual $C_f^{HBD}$ values, while the green solid lines (Figure 6) show predictions using calculated $C_f^{HBD}$ values from the correlation (Equation (7)). The predictive model with the calculated $C_f^{HBD}$ values provided a similar trend in predictions with the actual $C_f^{HBD}$ values (Figure 6), in which the ARD values from the calculated $C_f^{HBD}$ (gray-shaded rows, Table 2) are comparable to those estimated from the actual ones (entries 10–18, Table 2).

3.4. Limitation of the Predictive Model

According to predictive results in Section 3.1, the model (Equation (2)) provided a high ARD value for aqueous mixtures having a sigmoid function (entries 1–3, Table 2). Marcus reported [33,34] that the sigmoid trends were found in aqueous mixtures when microheterogeneity occurred. It is expected that the microheterogeneity phenomenon caused a high error in predictions because this phenomenon was not considered in the development of the model as mentioned in Section 2.2. Hunter basicity of HBA solvents ($\beta^H$, Table 2) can quantify the hydration shell strength in aqueous mixtures [35]. It was found that the sigmoid behaviors occurred in the aqueous mixtures that have low $\beta^H$ values ($\beta^H \leq 5.3$, entries 1–3, Table 2). Thus, the model (Equation (2)) is effective for predicting the aqueous mixtures having high $\beta^H$ values ($\beta^H \geq 5.3$).

4. Conclusions

In this work, a predictive model is proposed for estimating the solvatochromic polarity of electronic transition energy ($E_T$) for aqueous mixtures. The function form for $E_T$ values for aqueous mixtures can be adopted from the previous model for nonpolar-polar mixtures due to similar interactions and trends in the mixture $E_T$ values in both systems. The predictive model was validated by eighteen aqueous mixtures and was found to give a reliable $E_T$ value with an overall deviation of 2.1%. Three properties of pure components are basically needed for predictions: (i) $E_T$ values, (ii) gas-phase dipole moment and (iii) Kamlet-Taft acidity.

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Abbreviations

| AcOH | acetic acid |
| ACN | acetonitrile |
| ARD | average relative deviation, according to Equation (8) |
| BuOH | 1-butanol |
| DMF | dimethylformamide |
| DMSO | dimethyl sulfoxide |
| ETG | ethylene glycol |
| EtOH | ethanol |
| FA | formamide |
| GBL | gamma butyrolactone |
| GVL | gamma valerolactone |
HBA hydrogen bond acceptor
HBD hydrogen bond donor
iPrOH 2-propanol
Ind indicator
KT Kamlet–Taft solvatochromic parameter
MeOH methanol
Nile red 9-diethylamino-5-benzo(a) phenoxazinone indicator
NMP N-Methyl-2-pyrrolidone
Phenol blue N, N-dimethylindoloaniline indicator
PrOH 1-propanol
PYR 2-pyrrolidinone
Reichardt 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate indicator
T-BuOH tert-butyl alcohol
THF tetrahydrofuran

Latin symbols

\[ C_{\text{HBD}} \] HBD contribution factor, according to Equation (6)
\[ x \] mole fraction of solvent i

Greek symbols

\[ \beta^H \] Hunter basicity
\[ \alpha \] Kamlet–Taft acidity
\[ E_T \] electronic transition of solvent polarity
\[ E_{0,\text{Non}} \] non-HBD bonding electronic transition, according to Equation (6)
\[ \Delta E_{\text{T,mi}} \] relative normalized electronic transition energy, according to Equation (3)
\[ E_{\text{T,mi}} \] normalized electronic transition energy, according to Equation (4)
\[ E_T(\text{ideal}) \] ideal electronic transition energy, according to Equation (1)
\[ E_{\text{Cal}} \] calculated electronic transition energy, according to Equation (8)
\[ \mu \] gas-phase dipole moments
\[ \pi^* \] Kamlet–Taft dipolarity/polarizability

Superscript

0 pure property
N normalized property

Subscript

1 water, solvent type 1
2 HBA or HBD, solvent type 2
mix mixture property

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