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Supplementary material

SUPPLEMENTARY MATERIAL TO

The non-ideality in binary aqueous systems contributed to the different abilities of solvent entities incorporated in the solvation shell of methylene blue

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PREFERENTIAL SOLVATION (PS) MODEL

For binary mixtures consisting of solvents S_1 (water) and S_2 (organic solvent) and a solvatochromic indicator I, the proposed equilibria for the solvent exchange process are expressed as:

$$I(S_1)_2 + 2S_2 \rightleftarrows I(S_2)_2 + 2S_1 \quad \text{(S-1)}$$

In addition, the solvated complex (S_{12}) is formed by the interaction of solvent molecules with each other as follows:[1]

$$\mathrm{I}(S_1)_2 + S_2 \rightleftarrows \mathrm{I}\,(S_{12})_2 + S_1 \quad \text{(S-2)}$$

The fully solvated forms of solute I, in Eqs. S-1 and S-2, are shown as $I(S_1)_2$, $I(S_2)_2$, and $I(S_{12})_2$ with the solvents S_1, S_2, and S_{12}, respectively.[2,3] In this model, it is proposed that the solvated complex $I(S_{12})_2$ has new properties distinct from $I(S_1)_2$ and $I(S_2)_2$[11] and that the local composition of the solvation shell of a solute is present in equilibrium with the bulk composition of the solvent mixtures. It noted that the subscript 2 is interpreted as the number of solvent molecules participating in the exchange process in the solvation shell of the solvatochromic indicator and should not be confused with the total number of molecules that solvate the indicator.

It is assumed that in equilibrium, the mole fractions of the solvents involved in the local solvation shell of the indicator I ($x^L{}_1$, $x^L{}_2$, $x^L{}_{12}$) and the mole fractions in the bulk mixtures ($x^B{}_1$, $x^B{}_2$). Based on the mole fraction scale, the preferential parameters ($f_{2/1}$, $f_{12/1}$, and $f_{12/2}$) are determined from the solvent exchange equilibrium above:

$$f_{\underline{2}} = x_2^L (x_1^B)^2 / x_1^L (x_2^B)^2 \quad \text{(S-3)}$$

$$f_{\underline{12}} = x_{12}^L (x_1^B) / x_1^L (x_2^B) \quad \text{(S-4)}$$

$$f_{\underline{12}} = f_{\underline{12}} / f_{\underline{2}} = x_{12}^L (x_2^B) / x_2^L (x_1^B) \quad \text{(S-5)}$$

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The preferential solvation parameters fi/j indicate the ability of a solute to solvate with solvent i in the presence of solvent j. In fact, fi/j >1 indicates that the solute is preferably solvated in solvent i relative to solvent j and vice versa.[2]

The electronic transition energy, E_T, of a solvatochromic solute in a binary solvent mixture depends on the local composition of the solvation shell and is a weighted average of the E_T values corresponding to each of the solvation species in the solvation shell:

$$E_T = E_1x_1^L + E_2x_2^L + E_{12}x_{12}^L \tag{S-6}$$

The E_T values of the solute are estimated using E_1, E_2, and E_{12} values when the solute is solvated by S_1, S_2, and S_{12}, respectively. Finally, by introducing Eqs. 3 and 4 into Eq. 6 and assuming that the sum of all mole fractions in each region is equal to unity, the general equation to determine the E_T value is derived:

$$E_T = \frac{E_1x_1 + f_{2/1}E_2x_2 + f_{12/1}E_{12}x_1x_2}{\text{[illegible]}} \tag{S-7}$$

The parameters E_{12}, $f_{2/1}$, and $f_{12/1}$ can be calculated by a non-linear least square fitting of the experimental E_T values and the values from Eq. S-7.

TABLE S-I. The KAT parameters for different mole fraction, x_2, of organic solvents.

% cosolvent /parameters	Water-MeOH α	Water-MeOH β	Water-MeOH π*	Water-EtOH α	Water-EtOH β	Water-EtOH π*	Water-PrOH α	Water-PrOH β	Water-PrOH π*	Water-Dioxane α	Water-Dioxane β	Water-Dioxane π*
0	1.17	0.47	1.09	1.17	0.47	1.09	1.17	0.47	1.09	1.17	0.47	1.09
20	1.04	0.56	1.10	1.00	0.63	1.10	1.04	0.56	1.12	0.92	0.54	1.09
30	1.01	0.64	1.04	0.96	0.66	0.99	0.94	0.60	1.09	0.82	0.56	1.05
40	0.98	0.70	0.98	0.96	0.65	0.88	0.87	0.65	1.04	0.77	0.59	0.99
50	0.98	0.73	0.91	0.96	0.65	0.79	0.86	0.70	0.96	0.73	0.61	0.92
60	0.99	0.70	0.85	0.96	0.66	0.73	0.88	0.75	0.88	0.60	0.63	0.55
70	1.00	0.68	0.78	0.94	0.66	0.68	0.89	0.78	0.81	0.52	0.63	0.56
80	1.01	0.65	0.72	0.93	0.68	0.65	0.90	0.79	0.75	0.38	0.61	0.54
100	0.93	0.62	0.60	0.83	0.77	0.54	0.84	0.85	0.52	0.00	0.37	0.55

The values are obtained from Ref. 4

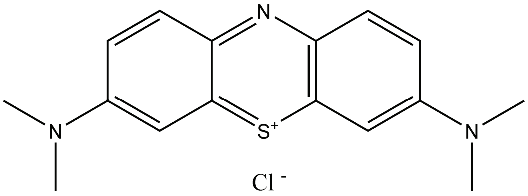

Fig. S-1. Structure of methylene blue (MB).

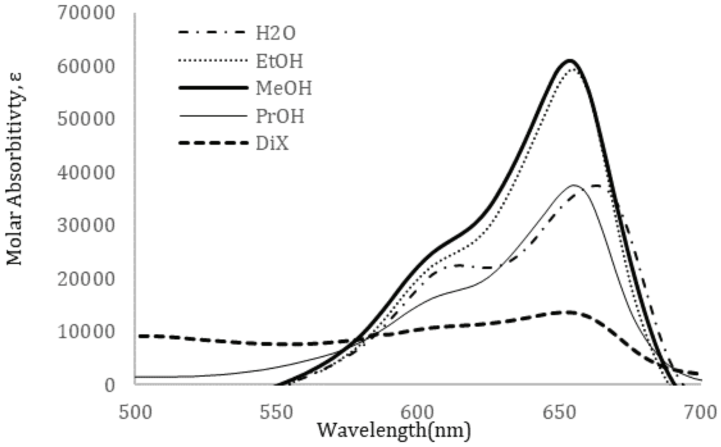

Fig. S-2. The electronic absorption spectrum of 3.13×10^{-5}mol.L^{-1} solution of MB in neat solvents at room temperature 25 °C.

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