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DMol3/COSMO-RS prediction of aqueous solubility and reactivity of selected Azo dyes: Effect of global orbital cut-off and COSMO segment variation

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ABSTRACT:

Aqueous solubility and reactivity of four azo dyes were investigated by DMol^3/COSMO-RS calculation to examine the effects of global orbital cut-off and COSMO segment variation on the accuracies of theoretical solubility and reactivity. The studied dyes are (E)-2,2'-((4-((2-chloro-4-nitrophenyl)diazenyl)-3-methylphenyl)azanediyl)diethanol [D1], (E)-2,2'-((4-((2,4-dinitrophenyl)diazenyl)-3-methylphenyl)azanediyl)diethanol [D2], (E)-2,2'-((4-((2,6-dichloro-4-nitrophenyl)diazenyl)-3-methylphenyl)azanediyl)diethanol [D3] and (E)-2,2'-((4-((2-chloro-4,6-dinitrophenyl)diazenyl)-3-methylphenyl)azanediyl)diethanol [D4]. The VWN-BP level of theory in conjunction with the double numerical basis set containing polarization function (DNP) was employed for the calculations. The aqueous solubility was calculated from the COSMO-RS data using the Cramer et al. solubility equation (CSE) and the general solubility equation (GSE) by Yalkowsky. The results showed that GSE calculated solubility (S_{GSE}) increases with orbital cut-off and reached optimum value at 5.5 Å orbital cut-off. S_{GSE} values obtained at 5.5 Å orbital cut-off for D1 and D3 are comparable to experimental values, while the best results were obtained for D2 and D4 at 4.5 Å cut-off. The CSE calculated solubility (S_{CSE}) showed no definite trend with cut-off variation but the best CSE cut-off for the dyes seemed to exhibit an inverse linear relationship with the molecular weights of the dyes. The reactivity of the dyes was enhanced in water and the minimum cut-off value for the reactivity study was 4.5 Å. Both the calculated solubility and reactivity indices generally showed low sensitivity to change in COSMO segment. We conclude that the DMol^3/COSMO-RS model is appropriate for predicting the aqueous solubility and reactivity of azo dyes and that the CSE and the GSE are reliable for solubility determination using COSMO-RS data, but their dependence on orbital cut-off differ.