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Exploring 1,2 and 1,n-alkanediols as hydrotropes: the impact of size and shape in the performance of hydrotropes

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PURPOSE OF THE ABSTRACT

Water is the most sustainable solvent following the Green Chemistry principles: it is readily available, non-flammable, non-toxic, cheap, and environmentally benign. Unfortunately, many compounds that present relevant properties and bioactivities are poorly soluble in water. Rather than using different solvents to process these compounds, hydrotropes can greatly expand the application scope of water as a solvent. Alkanediols are a class of di-alcohols widely used in the cosmetic, food, and pharmaceutical industries that can provide tunable solvent properties and act as hydrotropes to enhance the solubility of hydrophobic compounds.

Inspired by the recently proposed cooperative mechanism of hydrotrope [1], this work studies the impact of apolar volume and polar group position on the performance of hydrotropes. To do so, the ability of two different families of alkanediols (1,2-alkanediols and 1,n-alkanediols) to increase the aqueous solubility of syringic acid is investigated. Based on the Setschenow model, it is observed that in the dilute region (low hydrotrope concentration), the relative position of the hydroxyl groups of the alkanediols does not impact their performance both types of diols having a similar performance. Instead, their ability to increase the solubility of syringic acid correlates remarkably well with the size of their alkyl chains. However, this is not the case for larger hydrotrope concentrations, where 1,2-alkanediols are found to perform, in general, better than 1,n-alkanediols, as shown in Figure 1. Interestingly, for the 1,2 alkanediols series, the solubility is enhanced until 1,2-pentanediol, when the aggregation around the solute by the hydrotrope appears to be maximized. In fact, 1,2-hexanediol presents solubility enhancements similar to 1,4-butanediol, favoring hydrotrope-hydrotrope aggregation rather than hydrotrope-solute aggregation.

These contradictory findings are reconciled using theoretical and experimental techniques, namely the cooperative model of hydrotropy and chemical environment probes (Kamlet-Taft and pyrene polarity scales). It is found that the number of hydrotropes aggregated around a solute molecule does not increase linearly with the apolar volume of the former, reaching a maximum instead. This maximum is discussed in terms of competing solute-hydrotrope and hydrotrope-hydrotrope interactions. The results suggest that hydrotrope self-aggregation is more prevalent in 1,n-alkanediols, which negatively impacts their performance as hydrotropes.

The results reported in this work support the cooperative model of hydrotropy and, from a designing standpoint, show that hydrotropes should be designed taking into consideration not only their apolar volume but also their ability to stabilize their self-aggregation in water.

FIGURES

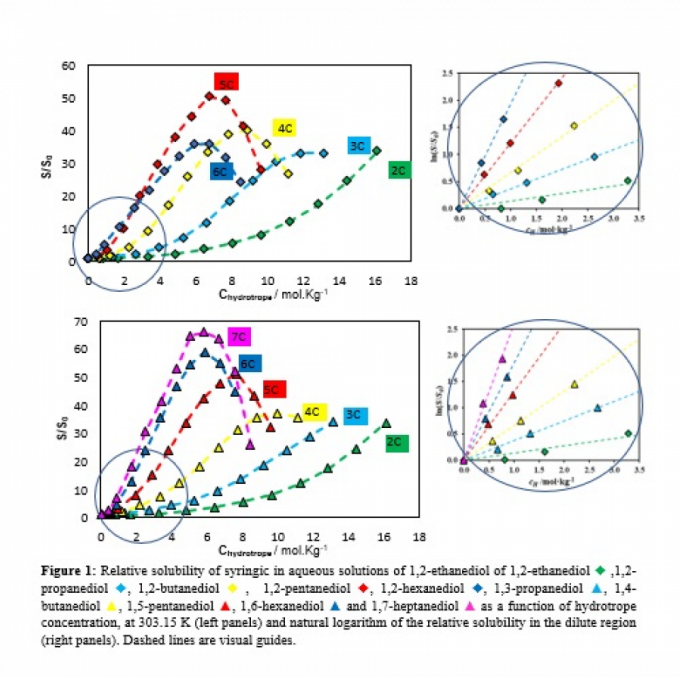

Figure 1: Relative solubility of syringic in aqueous solutions of 1,2-ethanediol ◆ ,1,2-propanediol ◆, 1,2-butanediol ◆ , 1,2-pentanediol ◆, 1,2-hexanediol ◆, 1,3-propanediol ▲, 1,4-butanediol ▲, 1,5-pentanediol ▲, 1,6-hexanediol ▲ and 1,7-heptanediol ▲ as a function of hydrotrope concentration, at 303.15 K (left panels) and natural logarithm of the relative solubility in the dilute region (right panels). Dashed lines are visual guides.

FIGURE 1

Figure 1

FIGURE 2

KEYWORDS

#hydrotropes | #alkanediols | #mechanismofaction | #apolarvolume

BIBLIOGRAPHY

[1] shimizu, s., matubayasi, n., phys. chem. chem. phys. 2016, 18, 25621–25628.