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Using solvatochromic probes to investigate intermolecular interactions in 1,4-dioxane/methanol/acetonitrile solvent mixtures

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ABSTRACT

UV–Vis absorption spectra of five solvatochromic probes namely, betaine (30), 4-nitrophenol, 4-nitroanisole, 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline, were obtained at 298.15 K in the binary systems 1,4-dioxane/methanol (MeOH) and 1,4-dioxane/acetonitrile (MeCN), and in the ternary system 1,4-dioxane/methanol/acetonitrile, in a total of 40 new solvent mixtures. Preferential solvation trends were assessed through the Bosch and Rosès formalism for the binary mixtures, and the extended model approach for the ternary mixture, thus allowing the setting up of a preferential solvation order for all entities present in solution, including solvent "complexes". Synergistic behaviors were spotted in most binary mixtures involving 1,4-dioxane but not in the ternary system which is dominated by a combination of contributions from the three underlying binary mixtures.
Kamlet-Taft parameters π^*, α and β were also computed for all 40 systems and their variation with composition was thoroughly examined. The addition of small amounts of 1,4-dioxane to the mixtures was seen to cause a significant variation in π^*, whereas on the other extreme, in dioxane rich mixtures, a large effect in α was observed, particularly for the system 1,4-dioxane/methanol.

1. Introduction

The characterization of solvents, as well as their influence upon reactivity and equilibria, has been an important recurrent subject both from a fundamental and an applied perspective [1].

Solvent mixtures build up in intricacy due to the increase in the number of components and therefore in the amount and complexity of interactions, but enable at the same time the fine-tuning of all sort of properties which are central for the understanding and prediction of the behavior of these media [2].

The study of solvent mixtures can be performed in different ways and using different approaches, some purely theoretical [3, 4], others involving experimental measures, such as density [5–8], refractive index [7–9], speed of sound [10, 11], viscosity [8, 12] or even IR and NMR spectroscopic measurements [13].

Another approach is based on the use of certain solutes which, in solution, behave as probes sensitive to different types of interactions, as described in various kinetic [14, 15], thermochemical [16–19] and spectroscopic studies [20–25].

Solvatochromism is a property related to the change in position, intensity and shape of the absorption bands of a given probe due to probe-solvent interactions. These interactions change the stabilization of the ground and first excited states of the probe molecule, either increasing or decreasing the energy difference between them, thus leading to a blue or red shift with increasing solvent polarity [2, 26, 27].

Solvatochromic probes have proven to be a valuable tool to measure the polarity of liquid media (and also of solids, glasses and surfaces [27]) not only because they allow the identification of distinct interactions, but also because they permit the quantification of those interactions [15, 19, 21, 22]. There are numerous solvatochromic scales built on the basis of different probes [28–35].

Following the rationale of our previous works [24, 25, 36], in the present study we have used the solvatochromic scales developed by Kamlet and Taft, namely, α, β and π^* [32, 34, 35].

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The π^* scale [35] is related with the solvent's dipolarity and polarizability and measures all non-specific probe-solvent interactions, comparing the probe's behavior in a particular solvent with that in two reference solvents, namely cyclohexane, for which $\pi^* = 0$, and dimethylsulfoxide, for which $\pi^* = 1$ - Eq. (1). This scale was initially based on the spectroscopic measurement of the $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of seven nitrosubstituted aromatic compounds [35].

$$\pi^*_{probe} = \frac{\left[\overline{\sigma}(Probe)_{Solvent} - \overline{\sigma}(Probe)_{Cyclohexane}\right]}{\left[\overline{\sigma}(Probe)_{DMSO} - \overline{\sigma}(Probe)_{Cyclohexane}\right]} \tag{1}$$

($\overline{\sigma}$ is the wavenumber of the probe's associated maximum energy transition band).

A few years later, the π^* scale was reviewed by Laurence and Nicolet [37–39] and later on by Abboud and Notario [40]. Laurence and Nicolet [39] proposed the use of a single probe, 4-nitroanisole (OMe), to determine π^*, and additionally, to avoid possible spectral interferences with OMe, of a secondary probe, *N*,*N*-dimethyl-4-nitroaniline (NMe_2). These two probes lead to the setting up of the π^*_{OMe} and π^*_{NMe2} sub-scales, respectively, whose values are obtained through Eqs. (2) and (3). As these values may differ slightly due to small differences in the way each probe interacts with the solvents, it has been common to use both probes to measure π^* and average the results into π^*_{avg} [25, 41].

$$\pi^*_{OMe} = \frac{\left[\overline{\sigma}(4-nitroanisole)_{Solvent} - 34.12\right]}{-2.4} \tag{2}$$

$$\pi^*_{NMe2} = \frac{\left[\overline{\sigma}(N,N-\text{dimethyl}-4-\text{nitroaniline})_{Solvent} - 28.18\right]}{-3.52} \tag{3}$$

The β scale measures specific probe-solvent interactions related with the basicity of hydrogen bond accepting solvents. This scale also compares β for the analyzed solvent with that in two reference solvents, cyclohexane ($\beta = 0$) and hexamethylfosforamide ($\beta = 1$), but in this case the measurement is based on the difference in wavenumber of two different probes instead of just one.

Due to significant differences between β values calculated using oxygen and nitrogen based probes, two sub-scales founded on different donor groups were proposed [37, 38]: β_{OH}, using 4-nitrophenol and 4-nitroanisole, and β_{NH2}, using 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline. Each β parameter can be calculated according to Eqs. (4) and (5):

$$\beta_{OH} = \frac{\left[1.0434\overline{\sigma}(4-nitroanisole)_{Solvent} - 0.57\right] - \overline{\sigma}(4-nitrophenol)_{Solvent}]}{2} \tag{4}$$

$$\beta_{NH2} = \frac{\left[0.9841\overline{\sigma}(N,N-dimethyl-4-nitroaniline)_{Solvent} + 3.49\right] - \overline{\sigma}(4-nitroaniline)_{Solvent}]}{2.759} \tag{5}$$

Finally, the α scale [34], which is conceptually very similar to the β scale previously described, measures the specific probe-solvent interactions related with the acidity of hydrogen bond donor solvents when compared with probe-methanol interactions (for which $\alpha = 1$). Again, two sub-scales were developed, using betaine (30) (Reichardt's dye), a probe sensitive to the solvent's acidity, and, either 4-nitroanisole (for α_{OMe}) or *N*,*N*-dimethyl-4-nitroaniline (for α_{NMe2}) as HBA probes [39]. α values can be calculated from Eqs. (6) and (7) and are usually averaged into α_{avg}.

$$\alpha_{OMe} = \frac{\left[1.873\overline{\sigma}(4-nitroanisole)_{Solvent} - 74.58\right] + \overline{\sigma}(betaine(30))_{Solvent}]}{6.24} \tag{6}$$

$$\alpha_{NMe2} = \frac{\left[1.318\overline{\sigma}(N,N-dimethyl-4-nitroaniline)_{Solvent} - 47.7\right] + \overline{\sigma}(betaine(30))_{Solvent}]}{5.47} \tag{7}$$

When solvatochromic probes are used to study solvent mixtures, it is expected that some degree of preferential solvation may occur. Through time several models [21, 42–45] have been developed to explain this phenomenon, among which the well-known and quite successful Bosch and Rosés preferential solvation model [20–22, 46–49], originally applied to binary mixtures. This model is based on a two-step solvent exchange process represented by the following equilibria ((a) and (b)):

$$\mathrm{I(S1)}_m + m\mathrm{S2} \rightleftharpoons \mathrm{I(S2)}_m + m\mathrm{S1} \tag{a}$$

$$\mathrm{I(S1)}_m + \frac{m}{2}\mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_m + \frac{m}{2}\mathrm{S1} \tag{b}$$

I represents the solute (or probe or indicator) molecule which is interacting with m molecules of either the pure solvents (S1 or S2) or of a “solvent complex” (S12) ensuing from the interaction of the two pure solvents. m is interpreted as the number of solvent molecules directly involved in the exchange process in the solvation microsphere of the solvatochromic indicator and affecting its transition energy and should not be confused with the total number of molecules that solvate the indicator [36, and references therein]. The whole exhange process occurs in the cybotatic region of the solute. As demonstrated in our previous works, only molecules in this region need to be considered by the model [24, 36].

Each equilibrium constant can be related to a preferential solvation parameter f. For example, parameter $f_{2/1}$ measures the likelihood of the indicator to be preferentially solvated by solvent S2 instead of by solvent S1 and can be related to the mole fractions of each solvent as follows (Eq. (8)):

$$f_{2/1} = \frac{x_2^s / x_1^s}{\left(x_2^0 / x_1^0\right)^m} \tag{8}$$

In this expression, x^s represents the mole fraction of the solvent in the cybotatic region of the solute and x^0 its mole fraction in the bulk solvent.