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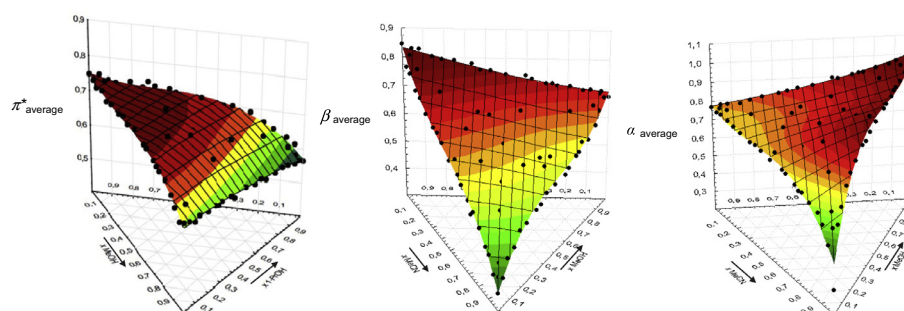
## UV–Vis spectroscopic study of preferential solvation and intermolecular interactions in methanol/1-propanol/acetonitrile by means of solvatochromic probes

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## HIGHLIGHTS

- Four solvatochromic probes were modeled by a preferential solvation model in MeOH/1-PrOH/MeCN.
- Synergistic effects and solvent “complexes” were identified.
- Solvation “scales” for each probe in the binary and ternary mixtures were set up.
- $\alpha$ ,  $\beta$ , and  $\pi^*$  values were obtained in the ternary mixture.
- Probe/solvent/solvent interactions were characterized and rationalized.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Solvatochromic UV–Vis shifts of four indicators (4-nitroaniline, 4-nitroanisole, 4-nitrophenol and *N,N*-dimethyl-4-nitroaniline) have been measured at 298.15 K in the ternary mixture methanol/1-propanol/acetonitrile (MeOH/1-PrOH/MeCN) in a total of 22 mole fractions, along with 18 additional mole fractions for each of the corresponding binary mixtures, MeOH/1-PrOH, 1-PrOH/MeCN and MeOH/MeCN. These values, combined with our previous experimental results for 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's betaine dye) in the same mixtures, permitted the computation of the Kamlet–Taft solvent parameters,  $\alpha$ ,  $\beta$ , and  $\pi^*$ . The rationalization of the spectroscopic behavior of each probe within each mixture's whole mole fraction range was achieved through the use of the Bosch and Rosés preferential solvation model. The applied model allowed the identification of synergistic behaviors in MeCN/alcohol mixtures and thus to infer the existence of solvent complexes in solution. Also, the addition of small amounts of MeCN to the binary mixtures was seen to cause a significant variation in  $\pi^*$ , whereas the addition of alcohol to MeCN mixtures always lead to a sudden change in  $\alpha$  and  $\beta$ . The behavior of these parameters in the ternary mixture was shown to be mainly determined by the contributions of the underlying binary mixtures.

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## Introduction

The use of electronic spectroscopy for the characterization of pure solvents through solvatochromic probes has been extensively

performed over the last decades, but fewer studies involved two solvents and even fewer addressed three or more component solutions [1–7]. The relevance of solvent mixtures becomes obvious considering their range of applications, which include modifications of solutes' solubility, tuning of solution physicochemical properties such as viscosity or polarity, and their use in separation processes like, for instance, in liquid chromatography, just to mention a few.

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The complexity of solvent/solvent interactions increases considerably with the number of components in the mixture. Although several models have been developed and used to address mixed solvents, most of them encompass only two components [8–20] or, at the most, to be able to deal with three components, they resort to fixed compositions, which make them in fact pseudo-three or more components mixtures [2–4] and therefore render it difficult to use information already available in the literature for two component mixtures and pure solvents. Our view is that this enhanced complexity instead of being a limitation constitutes, on the contrary, a window of opportunity to gain more information onto the underlying molecular phenomena.

Solvatochromic probes, whose spectroscopic behavior is strongly affected by solvents, allow a direct perception of the medium solvation ability and also on the involved specific and non-specific molecular interactions.

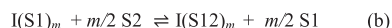
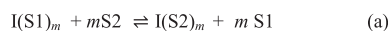
These probes allow two types of analysis: one based on the absorption band shift of the solvatochromic probes as a function of a component mole fraction, which permits the uncovering and relative quantification of preferential solvation phenomena; and, the other, centered on the determination of different polarity parameters such as the Kamlet–Taft solvatochromic parameters, via the measurement of the wavenumbers of one or more probes, which enables a detailed understanding of probe/solvent/solvent interactions.

In this work, and following our previous studies of the ternary mixture methanol/1-propanol/acetonitrile (MeOH/1-PrOH/MeCN) and of the underlying binary mixtures using Reichardt's betaine dye (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate) [21–23], four additional solvatochromic probes were employed to study the acidity, basicity and dipolarity/polarizability characteristics of these mixtures at 298.15 K, namely 4-nitroaniline, 4-nitroanisole, 4-nitrophenol and *N,N*-dimethyl-4-nitroaniline.

### Theoretical methods

#### Preferential solvation model

When one discusses the behavior of solvatochromic probes in mixtures, the possibility of occurrence of preferential solvation phenomena is naturally implicit. Several models that aim at explaining and quantifying these phenomena [8,10,24,25] have been proposed over time. Among them, Bosch and Rosés preferential solvation model [12,14–17,19,26] is one of the most successfully applied to study binary mixtures. It is based on a two-step solvent exchange process [16,17] represented by equilibria (a) and (b) (see Scheme 1).



Scheme 1.

where I represents the solute (indicator), S1 and S2 refer to the two pure solvents, S12 represents a new solvent entity ("a solvent complex") resulting from the interaction of solvents 1 and 2 and *m* is the number of solvent molecules involved in the exchange process in the cybotactic region of the solute, *i.e.*, in the solvation microsphere of the solvatochromic probe. Only the molecules in this region need to be accounted for by the model, as previously demonstrated by us [22]. *I*(Si/*j*) represents the indicator fully solvated by solvent *i* or *j*, or both.

Each corresponding equilibrium constant can be related to a preferential solvation parameter, *f*. In the case of equilibrium (a), the simplest situation of exchange of solvent molecules, *f*<sub>2/1</sub> measures the tendency of the indicator (or probe) to be preferentially solvated by solvent S2 rather than by solvent S1 and represents

the mole fraction distribution of the solvent between the solute's cybotactic region (*x*<sup>S</sup>) and the bulk mixed solvent (*x*<sup>0</sup>), Eq. (1).

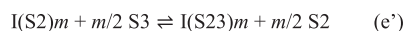
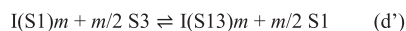
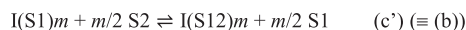
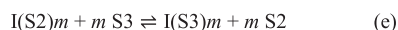
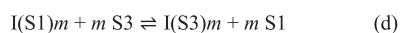
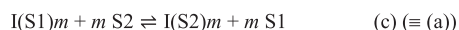
$$f_{2/1} = \frac{x_2^S/x_1^S}{(x_2^0/x_1^0)^m} \quad (1)$$

In Eq. (2), parameter *f*<sub>12/1</sub> quantifies the solvating ability of the S12 complex relative to solvent S1. *x*<sub>12</sub><sup>S</sup> stands, in turn, for the mole fraction of the binary S12 complex in the solvation microsphere of the probe.

$$f_{12/1} = \frac{x_{12}^S/x_1^S}{\sqrt{(x_2^0/x_1^0)^m}} \quad (2)$$

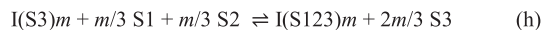
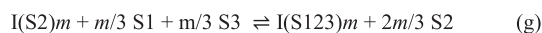
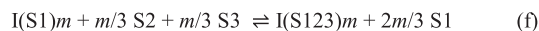
The occurrence of property values above or below the value of the solvatochromic properties for the pure components (provided that such variation exceeds experimental uncertainty) indicates the presence of significant solvent/solvent interactions and therefore implies a value of *m* greater than or equal to 2 (*i.e.*, denotes a mixture with synergistic effect [22]).

The extension of the Bosch and Rosés preferential solvation model to ternary mixtures was previously presented in detail and applied by these authors [22]. This extension implied an increase in the number of implicit equilibria involved and, thus, of the complexity of the underlying mathematical treatment. It entailed the simultaneous consideration of balances (c) and (c'), (d), and (d'), and (e) and (e') which are the transposition for a ternary mixture of the general two-stage solvent exchange model (see Scheme 2).



Scheme 2.

In the ternary mixture there is also the possibility of formation of a ternary solvating complex with the solute probe *I*(S123), which can be translated by the following equilibria (see Scheme 3).



Scheme 3.

For each of these equilibria, as in the original Bosch and Rosés model, it is possible to define an equilibrium constant that correlates the solvent's mole fraction in the solvation microsphere of the probe with its mole fraction in the bulk. These equilibrium constants can be once again linked with preferential solvation parameters, *f*.

In the case of formation of a ternary complex interacting with the probe, the preferential solvation of S123 relative to solvent S1 can be expressed by:

$$f_{123/1} = \frac{x_{123}^S/x_1^S}{\sqrt[3]{(x_2^0/x_3^0)^m}} \quad (3)$$

where  $x_{123}^S$  represents the mole fraction of the ternary S123 complex.

A given solvatochromic property ( $Y$ ) in a mixture can be expressed as the sum of the contributions of each solvent entity in the solute's cybotactic region, which is given by the product of the corresponding mole fractions by the property value for each entity,  $Y_i$ :

$$Y = Y_1 x_1^S + Y_2 x_2^S + Y_3 x_3^S + Y_{12} x_{12}^S + Y_{13} x_{13}^S + Y_{23} x_{23}^S + Y_{123} x_{123}^S \quad (4)$$

Mole fractions in the cybotactic region must then be converted into known variables on the basis of preferential solvation parameters,  $f$ , already defined, considering that the sum of all mole fractions in the cybotactic region and in the solvent's bulk should be equal to one. After making all the mole fraction conversions and the necessary simplifications [22], the following preferential solvation expression is obtained:

$$Y = \frac{Y_1 (x_1^0)^m + Y_2 f_{2/1} (x_2^0)^m + Y_3 f_{3/1} (x_3^0)^m + Y_{12} f_{12/1} (x_1^0 x_2^0)^{\frac{m}{2}} + Y_{13} f_{13/1} (x_1^0 x_3^0)^{\frac{m}{2}} + Y_{23} f_{23/1} (x_2^0 x_3^0)^{\frac{m}{2}} + Y_{123} f_{123/1} (x_1^0 x_2^0 x_3^0)^{\frac{m}{3}}}{(x_1^0)^m + f_{2/1} (x_2^0)^m + f_{3/1} (x_3^0)^m + f_{12/1} (x_1^0 x_2^0)^{\frac{m}{2}} + f_{13/1} (x_1^0 x_3^0)^{\frac{m}{2}} + f_{23/1} (x_2^0 x_3^0)^{\frac{m}{2}} + f_{123/1} (x_1^0 x_2^0 x_3^0)^{\frac{m}{3}}} \quad (5)$$

Values of  $f_{ij}$  close to 1 correspond to an ideal mixture, i.e., a mixture with no preferential solvation and therefore no synergism. Values higher than 1 indicate that the probe is preferentially solvated by solvent  $i$  rather than by solvent  $j$ . Conversely, the probe is better solvated by solvent  $j$  if  $f_{ij}$  is lower than 1.

Since all parameters relate to the same solvent, S1, it is feasible to build preferential solvation scales for the mixture constituents (Si, Sij and Sijk) in terms of the measured solvatochromic property,  $Y$ .

#### Solvatochromic parameter calculations

The solvatochromic indicators used in this work are represented in Fig. 1.

Kamlet and Taft [27–31] originally proposed a set of different solvatochromic probes and reference processes to define solvent polarity scales based on average values for each type of polarity parameter. Later on, Laurence and Nicolet revised the original reference processes/probes proposing a simpler set, using a total of five probes [32,33], in order to overcome possible blurring effects related to averaging. This methodology has since been employed by other authors in the context of the study of solvent mixtures [34–36].

$\pi^*$ , a scale of solvent dipolarity/polarizability, measures all possible non-specific solute/solvent intermolecular interactions, particularly the ease of distortion of the solvent's electronic cloud in the presence of an electrical field (arising from the proximity of another electronic cloud). Two probes, 4-nitroanisole

(A) and  $N,N$ -dimethyl-4-nitroaniline (B) have been used to establish two different  $\pi^*$  scales, each one based on one of the probes, respectively  $\pi_{\text{OMe}}^*$  (Eq. (6)) and  $\pi_{\text{NMe}_2}^*$  (Eq. (7)). These equations use the wavenumber,  $\bar{\sigma}$  (in  $\text{kK} = 10^3 \text{ cm}^{-1}$ ), of the probe's associated maximum energy transition band. The two scales are then normalized using two reference solvents: on one end cyclohexane, for which  $\pi^* = 0$  (since this solvent is unable to perform any type of specific interactions and has the lowest capacity to suffer distortion of its electronic cloud) and, at the other end, dimethylsulfoxide, for which  $\pi^* = 1$ .

$$\pi_{\text{OMe}}^* = \frac{\bar{\sigma}(\text{A}) - 34.12}{-2.4} \quad (6)$$

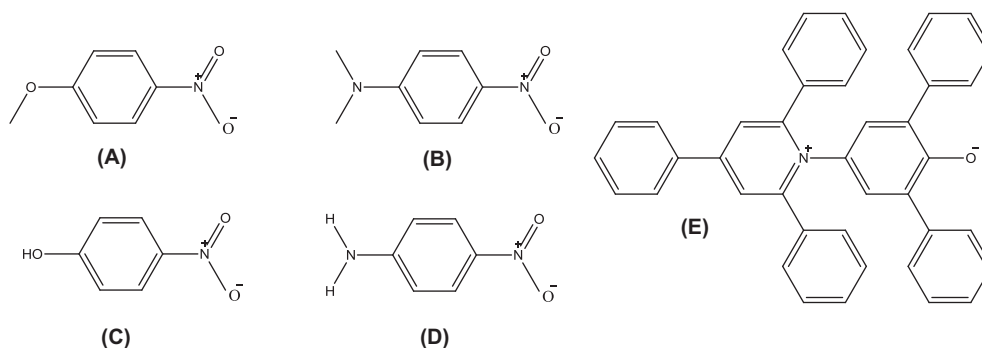
$$\pi_{\text{NMe}_2}^* = \frac{\bar{\sigma}(\text{B}) - 28.18}{-3.52} \quad (7)$$

The Kamlet–Taft  $\beta$  parameter is a measure of specific solute/solvent interactions related to the hydrogen bond acceptor (HBA) basicity characteristics of the solvent. Its determination was also based on the assumptions set out initially by Kamlet and Taft and their solvatochromic comparison method [28]. In this case the proposed methodology consists of using the wavenumber difference between two or more homomorphic probes: one, a hydrogen bond donor (HBD) probe, and the other, a probe unable to perform such interactions. Years later, this scale was also partly re-designed by Nicolet and Laurence [32,37], who recommended the use of pairs of probes to determine  $\beta$  values: the first pair comprised 4-nitroanisole (A) and 4-nitrophenol (C), with donor capacity via  $-\text{OH}$  group; and the second one involved  $N,N$ -dimethyl-4-nitroaniline (B) and 4-nitroaniline (D), with donor ability via  $-\text{NH}$  group. Eqs. (8) and (9) represent the two  $\beta$  scales resulting from the use of these two homomorphic pairs, i.e.,  $\beta_{\text{OH}}$  and  $\beta_{\text{NH}_2}$ , respectively. Both scales are standardized to give a value of 1 in hexamethylphosphoramide, using the probes' wavenumbers (in  $\text{kK}$ ):

$$\beta_{\text{OH}} = \frac{[1.0434\bar{\sigma}(\text{A}) - 0.57] - \bar{\sigma}(\text{C})}{2} \quad (8)$$

$$\beta_{\text{NH}_2} = \frac{[0.9841\bar{\sigma}(\text{B}) + 3.49] - \bar{\sigma}(\text{D})}{2.759} \quad (9)$$

The Kamlet–Taft  $\alpha$  parameter is also a measure of specific solute/solvent interactions but this time related to the solvent's HBD acidity characteristics. The calculation of  $\alpha$  is also performed on the ba-



**Fig. 1.** Solvatochromic probes used: 4-nitroanisole (A),  $N,N$ -dimethyl-4-nitroaniline (B), 4-nitrophenol (C), 4-nitroaniline (D), 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (E).

sis of the solvatochromic comparison method, using in this case a HBA probe and a probe sensitive to the solvent's acidity, in this case the Reichardt's dye (*E*), known as  $E_T(30)$  [38,39], or merely betaine (30).  $\alpha$  values are then computed using the two following pairs of probes: 4-nitroanisole (*A*)/2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (*E*) and *N,N*-dimethyl-4-nitroaniline (*B*)/2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (*E*), giving rise to the  $\alpha_{\text{OMe}}$  and the  $\alpha_{\text{NMe}_2}$  scales, standardized to give a value of 1 in methanol (with  $\bar{\sigma}$  also in kK) and represented by Eqs. (10) and (11), respectively:

$$\alpha_{\text{OMe}} = \frac{[1.873\bar{\sigma}(A) - 74.58] + \bar{\sigma}(E)}{6.24} \quad (10)$$

$$\alpha_{\text{NMe}_2} = \frac{[1.318\bar{\sigma}(B) - 47.7] + \bar{\sigma}(E)}{5.47} \quad (11)$$

## Experimental

UV–Vis spectroscopic analysis was performed at 298.15 K in a Jasco V-530 spectrophotometer, equipped with a jacketed cell module which allowed a thermostatic control from a recirculating water bath with an uncertainty of  $\pm 0.1$  K. A pair of matched quartz analytical cells of 1 cm path length was used in all measurements.

Chemicals employed are listed in Table 1 and were used as received. All solvents were HPLC grade and their purity was confirmed by ascertaining that values obtained for measured physical properties for the pure solvents (densities and refractive indices) were in agreement with literature values [40,41].

Mixtures were carefully prepared by mass in a precision balance with an uncertainty in mass of  $\pm 2 \times 10^{-4}$  g. Precautions were taken to avoid evaporation and contamination by humidity. No correction was made for the water content in the alcohol in the calculation of the mole fractions.

Each solvatochromic probe was pre-dissolved in the mixtures, and the concentration was adjusted by adding more solvent mixture or solvatochromic probe in order to obtain absorbance values in the range 0.6–0.9.

Reported wavenumbers result from, at least, an average of three individual experiments and always presented a relative standard deviation of less than 0.14%.

## Results and discussion

Table S1 (in Supplementary Material) summarizes the experimental wavenumbers corresponding to the absorption maxima obtained for each of the solvatochromic probes in the three binary mixtures at 298.15 K. The same information is presented in Table S2, for the ternary mixture.

Fig. 2 shows the variation of the wavenumber with the co-solvent mole fraction for each of the four solvatochromic probes used in the three binary mixtures. Solid lines correspond to the best fitting functions as given by the Bosch and Rosés model. Adjusted

parameters are compiled in Tables S3–S6 (in Supplementary Material). Bold values were not determined by nonlinear iteration fitting but by subsequent calculations [22].

As explained in Ref. [22] after the first fit, outliers were identified by the concomitant use of various statistical criteria, namely the Cook's distance, the studentized deleted residuals and the DFFITS parameter. All the spotted anomalous points were not used in the final iteration. Microsoft Excel® and Microsoft Excel add-in SOLVERSTAT® [42] were used for the computation of the model's parameters and their associated uncertainties.

### Preferential solvation analysis

Fig. 2a and Table S3 (in Supplementary Material) show that the fit of 4-nitroanisole in MeOH/MeCN has a relatively low  $r^2$ , but the magnitude of  $f_{2/1}$  ( $>2$ ) clearly reveals that this probe is preferably solvated by MeCN rather than by MeOH. Mancini et al. [43] working with the same indicator and mixture, suggested the formation of a solvent/solvent complex with a wavenumber value lower than that of the pure components. However, these authors have only used 9 mole fractions and did not indicate the associated uncertainties, which in this case is a determinant factor given the small variability of wavenumbers.

A close inspection of  $f_{2/1}$  values in Table S3 indicates that for the MeOH/1-PrOH mixture, MeOH is the predominant species in the vicinity of the probe, whereas in the case of 1-PrOH/MeCN, MeCN appears as the solvent that best solvates 4-nitroanisole.

The analysis of all parameters show that no solute/solvent/solvent synergistic interactions occur in any of these mixtures, being the preferential solvation order for this probe the following: MeCN > MeOH > 1-PrOH. On the other hand, the estimated wavenumbers for the pure solvents are in good agreement with the experimental values.

The analysis of the fitting parameters for *N,N*-dimethyl-4-nitroaniline (Fig. 2b and Table S4) reveals that, in comparison with 4-nitroanisole, there are two main differences in the observed behaviors: the solvating order in MeOH/1-PrOH is reversed, perhaps as a result of the additional  $\text{CH}_3$  group in 1-PrOH, and, on the other hand, for the mixture MeOH/MeCN there are some mole fractions ( $0.5 < x_{\text{MeCN}} < 0.9$ ) whose wavenumber value is lower than that of the pure components, an evidence of a synergistic effect. This negative synergistic behavior can be rationalized in terms of a possible probe–solvent S12 complex interaction, with a lower ability to perform non-specific interactions than the pure solvents. This type of interaction is important in view of the impossibility of this probe to perform specific interactions.

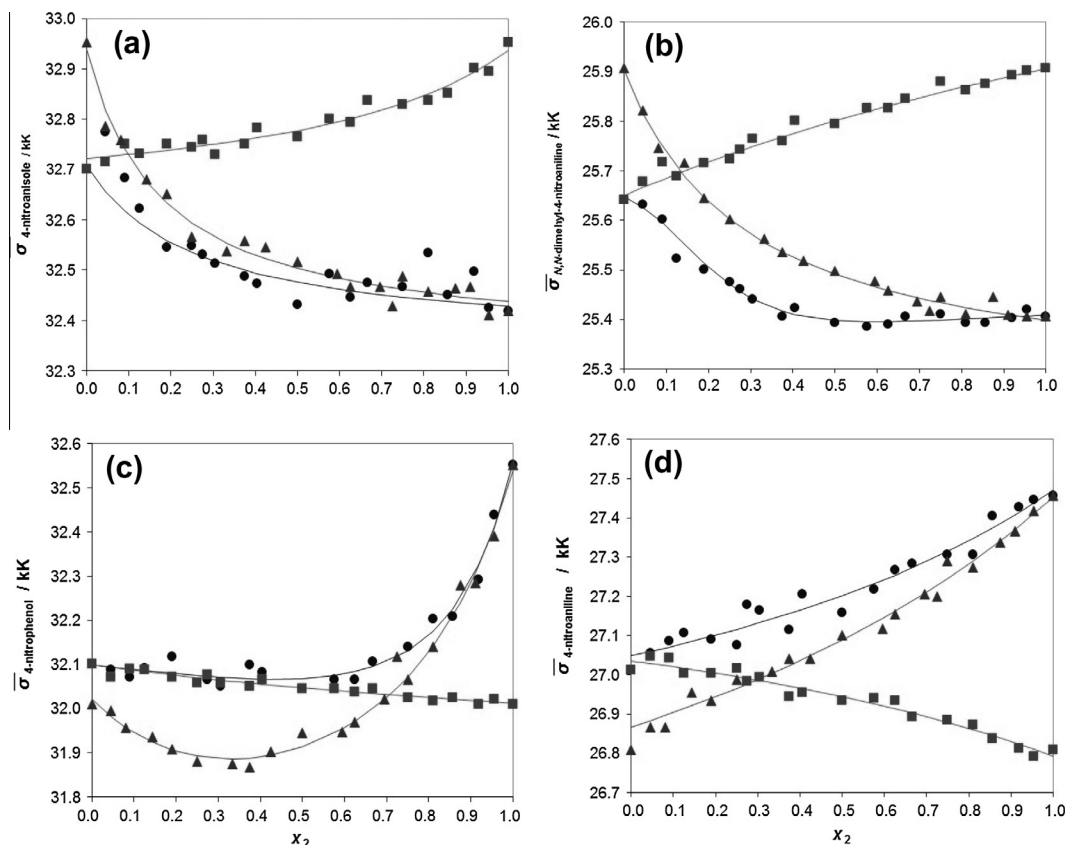
The choice of the model with  $m = 2$  for this mixture is based on the existence of property values below the values of the pure components and which cannot be accounted for with a model with  $m = 1$ . Nonetheless, the low statistical significance of the parameters, especially of  $f_{12/1}$ , shows that this system is a limit case for the consideration of a negative synergism.

From the computed coefficients, it is difficult to infer any chemical information about the S1/S2 complex. All one can say is that the best solvating solvent for *N,N*-dimethyl-4-nitroaniline is MeCN. Regarding the S1/S2 complex, however, there is some indication in the literature that it may in fact be formed. Mancini et al., using a very similar probe, *N,N*-diethyl-4-nitroaniline, also detected wavenumber values smaller than those for the pure components for some mole fractions [43]. This situation was attributed to the formation of a HBA/HBD complex. As previously mentioned for 4-nitroanisole, the referred study reports again relatively high associated uncertainties and uses only a small number of mole fractions but the observed synergism is present in a wider range of mole fractions,  $0.3 < x_{\text{MeOH}} < 0.6$ . From the information gathered, it is possible to say that *N,N*-dimethyl-4-nitroaniline tends to be preferentially solvated in the order

**Table 1**  
Brand and stated purity of chemicals used in the spectroscopic measurements.

	Source	Purity (%)
Methanol	Riedel de H��en	99.9
1-Propanol	Aldrich	99
Acetonitrile	Aldrich	99.5
4-Nitroaniline	Aldrich	99
4-Nitroanisole	TCI	98
4-Nitrophenol	Merck	99.5
<i>N,N</i> -dimethyl-4-nitroaniline	TCI	98
Betaine (30) (Reichardt's dye)	Fluka	>98.5





**Fig. 2.** Variation of the wavenumbers of probes (a) 4-nitroanisole, (b) *N,N*-dimethyl-4-nitroaniline, (c) 4-nitrophenol, and (d) 4-nitroaniline with the mole fraction of the second component in the studied binary solvent mixtures, at 298.15 K: (■) MeOH/1-PrOH, (●) MeOH/McCN, (▲) 1-PrOH/McCN. All solid lines represent the best fitting functions resulting from the application of the Bosch and Rosés preferential solvation model.

MeCN > 1-PrOH > MeOH > MeOH/McCN complex. Again, estimated  $\bar{\sigma}$  values are very similar to experimental ones.

The behavior of 4-nitrophenol in MeOH/McCN, shows the same type of singularities as that of *N,N*-dimethyl-4-nitroaniline (vd. Fig. 2c and Table S5). A slight negative synergism ( $0.25 < x_{\text{MeCN}} < 0.62$ ) is observed which implies that only model with  $m = 2$  is able to explain the variation of the wavenumber of this probe with composition. There are, however, high uncertainties associated with the coefficients, particularly those related with  $f_{12/1}$ , making it impossible to accurately interpret the precise nature of the postulated solvent/solvent complex.

The same is not true, however, for 1-PrOH/McCN, wherein the negative synergism is clearly visible in the mole fraction region between 0.04 and 0.62 in MeCN, thus evidencing the interaction between the complex formed by the two solvents and the probe. Moreover, this S1/S2 complex preferably solvates this probe when compared to either 1-PrOH or MeCN ( $f_{12/2} = 4.1$  and  $f_{12/1} = 3.3$ ).

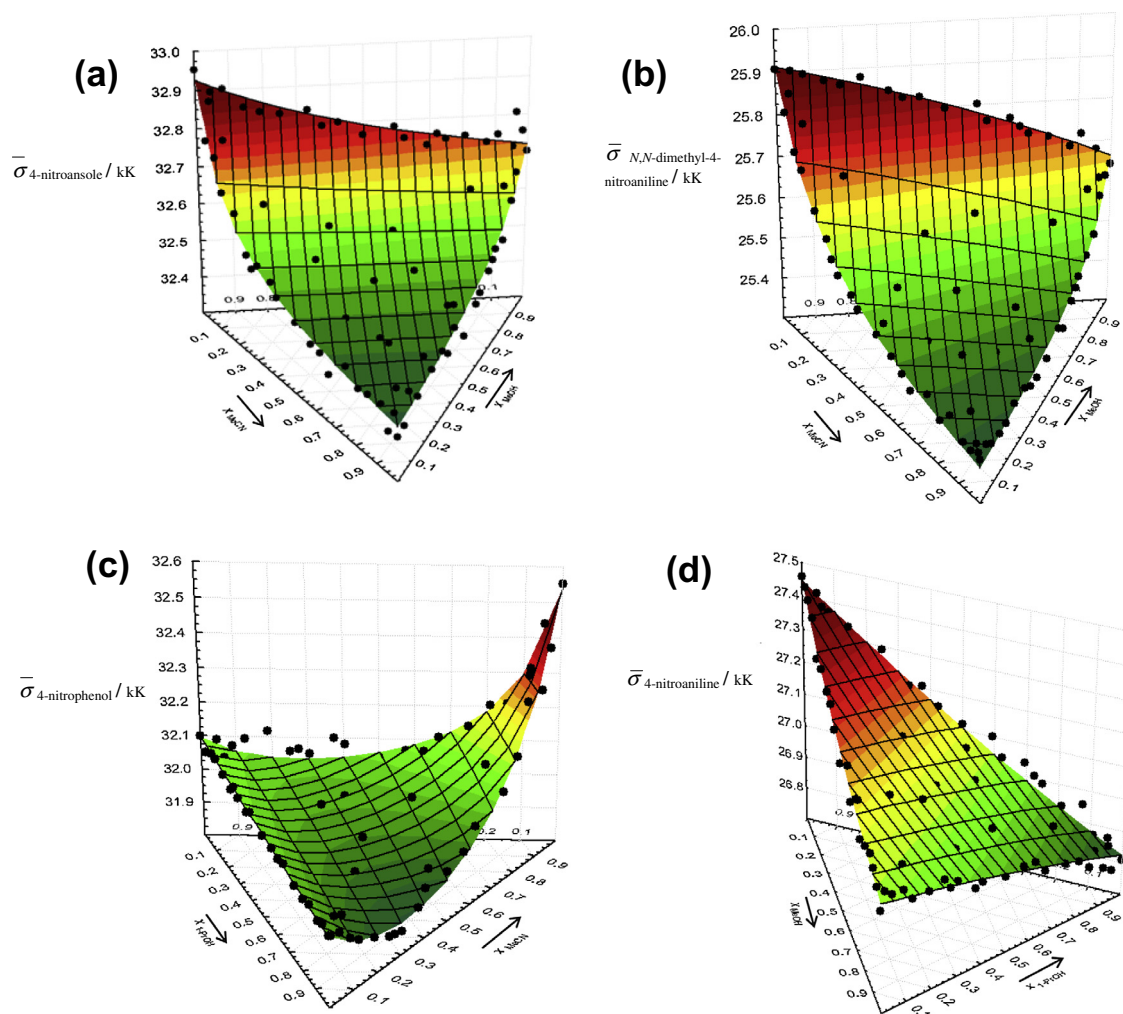
The mixture MeOH/1-PrOH, despite showing the lowest coefficient of determination of the fit, shows a nearly ideal behavior (with a slight preferential solvation of the probe by 1-PrOH). 4-nitrophenol is characterized by its capability to establish specific interactions through the -OH group. In hydroxylic solvents-McCN mixtures, the negative synergistic behavior can be due to the higher polarity of MeCN-ROH complexes, which leads to a bathochromic shift of the probe's absorption band, i.e., to a lower ground-state stabilization, leading to a lower transition energy and therefore to a wavenumber smaller than what would be expected if the behavior was ideal.

In summary, the order of preferential solvation for 4-nitrophenol is: 1-PrOH/McCN complex > 1-PrOH > MeOH > MeOH/McCN complex > MeCN.

The analysis of Fig. 2d and Table S6 reveals that in MeOH/McCN, despite its slightly worse statistical fitting by comparison with the remaining mixtures, 4-nitroaniline is best solvated by the alcohol component ( $f_{2/1} < 1$ ). In the case of MeOH/1-PrOH, given the value of  $f_{2/1}$ , the probe is also preferably solvated by MeOH, while in 1-PrOH/McCN the alcohol shows better solvating ability than MeCN. The results for this probe show that no synergistic behavior is observed for any of the mixtures. MeOH and 1-PrOH, which can interact with 4-nitroaniline through their -OH groups, solvate this probe better than MeCN unable to establish this type of interactions. The preferential solvation order is thus: MeOH > 1-PrOH > MeCN. The computed  $\bar{\sigma}$  values for the pure solvents agree with the experimental values within 0.2%.

Fig. 3 shows the variation of the wavenumbers for the four solvatochromic probes in the ternary mixture with solvent composition, and also the fitting surfaces generated by Eq. (5). The corresponding solvation models' parameters are shown in Tables S7–S10 of Supplementary Material. In general, Fig. 3 shows a very good fit between experimental results and predicted ternary surfaces.

Table S7 presents the ternary model fitting parameters for 4-nitroanisole with and without the terms resulting from the ternary contribution. The need to apply a ternary model with  $m = 2$  even when the underlying binary mixtures are explained by  $m = 1$  is due to the fact that the ternary mixture can exhibit synergism even if there is no synergism in the binary mixtures. The application of the preferential solvation model shows, however, that the ternary component is not significant in the ternary mixture (the value of  $f_{123/1}$  is zero), and it is then clear that this probe does not detect any probe-solvent interaction involving simultaneously the three solvents. Interestingly, the “binary” solvation parameters



**Fig. 3.** Variation of the wavenumber of the probes (a) 4-nitroanisole, (b) *N,N*-dimethyl-4-nitroaniline, (c) 4-nitrophenol, (d) 4-nitroaniline with solvent composition in the studied ternary mixture, at 298.15 K and respective surfaces predicted by the solvation model.

recalculated by the ternary solvation model are very similar to those previously determined by the binary model (vd. Table S7 vs. Table S3). Also, the equations built with the parameters in Table S7 reproduce the probe's wavenumbers in each of the pure solvents.

The analysis of the preferential solvation model applied to *N,N*-dimethyl-4-nitroaniline shows that the consideration of a ternary complex (Table S8) is irrelevant from a statistical point of view for the modeling process of the ternary mixture and therefore, for this probe, there is again no visible probe–solvent interaction involving simultaneously all the solvents.

The “binary” solvation parameters recalculated by the ternary model confirm, once more, the values in Table S4 obtained using the binary model. The only exception is the relative position of the MeOH/MeCN solvating complex *vis-à-vis* the other solvents. However, the standard deviation associated with  $f_{12/1}$  calculated from the binary model is greater than the parameter itself (Table S4) making it meaningless. Thus, the ternary mole fractions allow us to reassess the relative position of this complex and to establish the following descending order of preferential solvation for *N,N*-dimethyl-4-nitroaniline: MeCN > MeOH/MeCN complex > 1-PrOH > MeOH.

The analysis of the application of the preferential solvation model to 4-nitrophenol shows that the ternary component (Table S9) has no statistical significance, suggesting again that, for this probe, there seems to be no interaction involving simultaneously MeOH, 1-PrOH and MeCN and the probe itself. The recal-

culated solvation parameters values using the ternary solvation model show a reduction of the uncertainties previously associated with several of the parameters in Table S5. A close inspection of Table S9 makes clear that 4-nitrophenol is preferably solvated by the MeOH/MeCN complex and right after by the 1-PrOH/MeCN complex. In what regards the pure solvents, the order of solvation is difficult to assess in view of the computed uncertainties. However, their solvation ability towards this probe should be similar since the solvation parameters are very close to one.

The preferential solvation model applied to 4-nitroaniline shows that the ternary component has, like in previous cases, no statistical/physicochemical significance ( $f_{123/1}$  is virtually zero), and therefore there are no probe/S1/S2/S3 interaction. When the “binary” solvation parameters values are recalculated using the ternary solvation model, the obtained values confirm those resulting from the application of the model to the underlying binary mixtures and lead to the same preferential solvation order, *i.e.*: MeOH > 1-PrOH > MeCN. Similarly to the other three probes, the ternary solvation model for 4-nitroaniline gives an estimate  $\bar{\sigma}$  value for the pure solvents very close to that predicted by the model applied to the binary mixtures.

#### Kamlet–Taft parameters

Tables S11 and S12 (in Supplementary Material) assemble the calculated Kamlet–Taft parameters for the binary and ternary mixtures, respectively.

The  $\pi_{\text{OMe}}^*$  parameter based on 4-nitroaniline (Fig. 4a) reveals that the mixture MeOH/1-PrOH behaves almost ideally, with slightly positive deviations occurring especially in 1-PrOH rich regions ( $x_{1-\text{PrOH}} > 0.8$ ). The mixture MeOH/MeCN shows large (positive) deviations for intermediate mole fractions ( $x \approx 0.5$ ), but also negative deviations in the vicinity of the pure compo-

nents. The mixture 1-PrOH/MeCN, in turn, shows a strong positive deviation particularly evident for mole fractions close to 0.2 in MeCN.

The  $\pi_{\text{NMe}_2}^*$  parameter based on *N,N*-dimethyl-4-nitroaniline (Fig. 4b) shows for MeOH/1-PrOH a very small negative deviation from ideality, whereas MeOH/MeCN exhibits a positive deviation

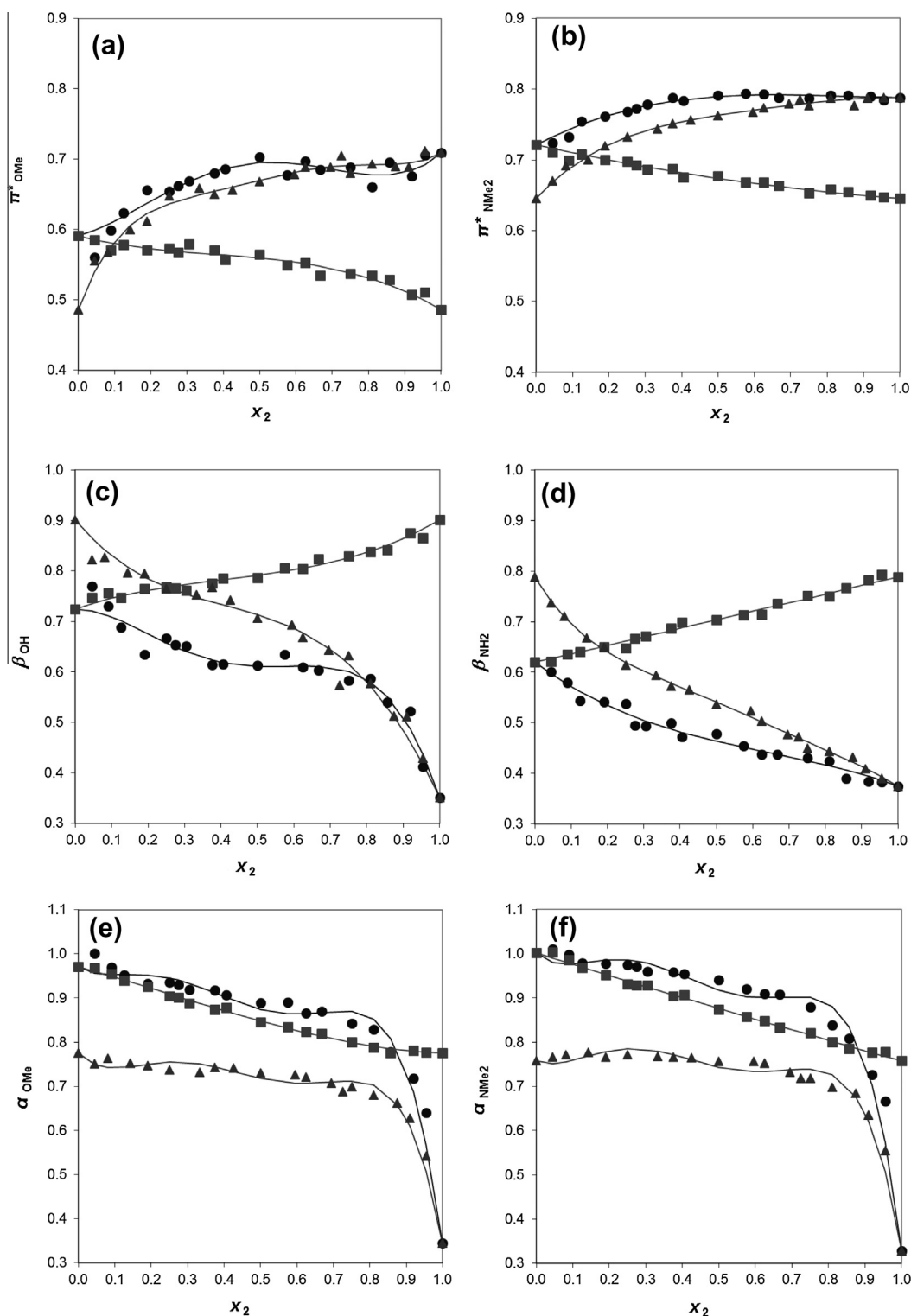


Fig. 4. Variation of the Kamlet–Taft parameters as a function of composition in the studied binary solvent mixtures, at 298.15 K: (■) MeOH/1-PrOH, (●) MeOH/MeCN, (▲) 1-PrOH/MeCN. Solid lines represent empirical polynomial fitting functions.



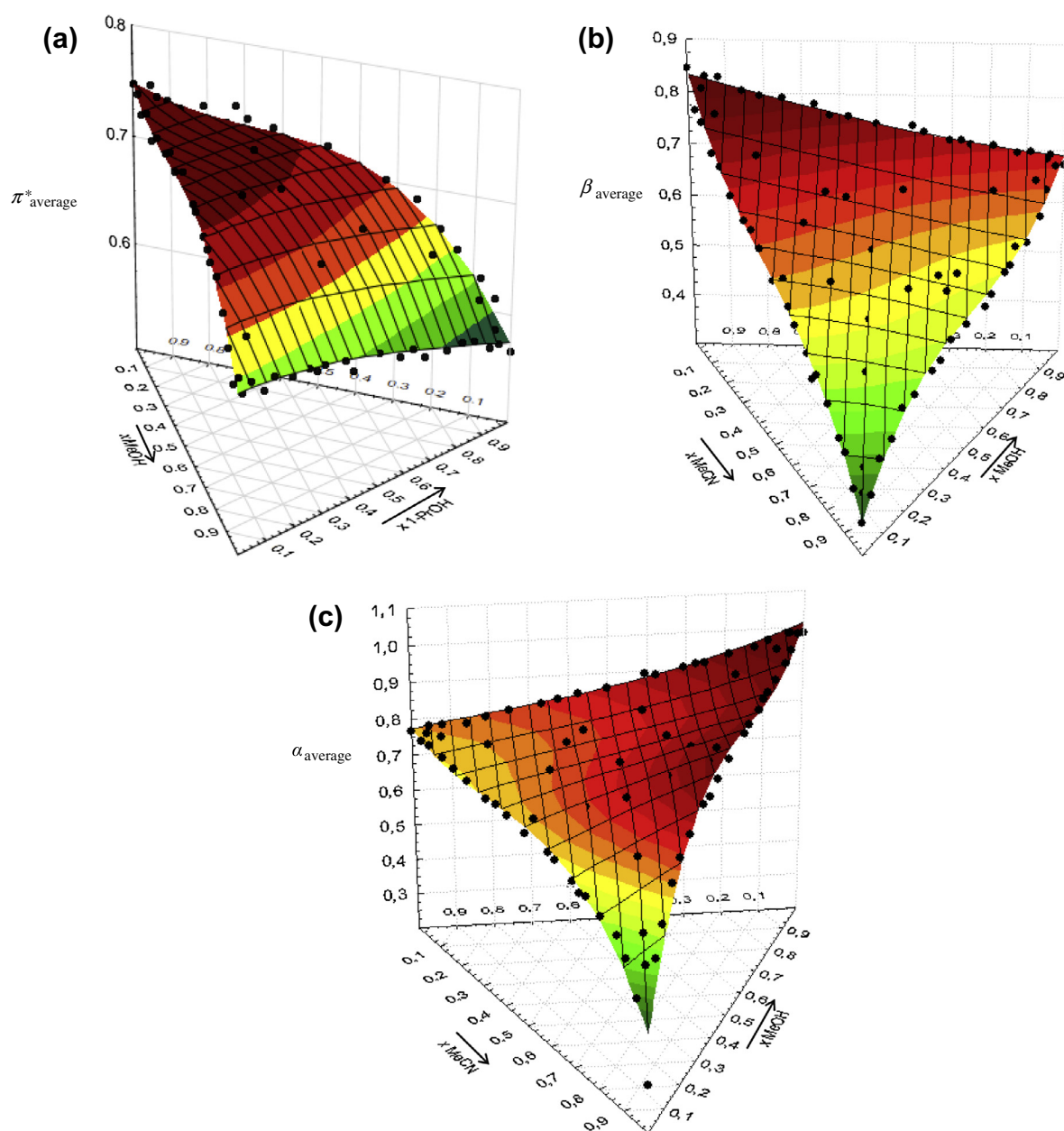
as seen also with the previous probe, but this time throughout the whole composition range, although higher for intermediate mole fractions. The mixture 1-PrOH/MeCN shows, once more, a strong positive deviation, this time more pronounced for mole fractions close to 0.3 in MeCN.

$\pi^*$  values for the ternary mixture are presented in Fig. 5a and correspond to the arithmetic average of the two  $\pi_{\text{OMe}}^*$  and  $\pi_{\text{NMe}_2}^*$  scales. The analysis of the ternary mole fractions clearly exposes deviations from ideality. These deviations, can however, be largely explained by the binary contributions.

The analysis of the  $\beta$  parameter based on the pair 4-nitrophenol/4-nitroanisole ( $\beta_{\text{OH}}$ ) (Fig. 4c) reveals an ideal behavior for MeOH/1-PrOH up to about  $x_{1-\text{PrOH}} = 0.4$ . From this point on the mixture shows a slightly negative deviation from ideality. For MeOH/MeCN and 1-PrOH/MeCN extensive positive deviations are

observed, with maxima occurring at MeCN mole fractions between 0.6 and 0.8. In alcohol/MeCN mixtures, as the alcohol mole fraction increases, the “basic” character of the mixture due to the presence of –OH groups rapidly increases, leading to higher deviations from ideality.

The behavior of  $\beta$  obtained from the pair 4-nitroaniline/*N,N*-dimethyl-4-nitroaniline ( $\beta_{\text{NH}_2}$ ) (Fig. 4d) shows that the mixture MeOH/1-PrOH displays an ideal behavior, while the other two mixtures exhibit negative deviations, with a maximum departure from ideality at mole fractions of 0.25 in MeCN. However, when small amounts of alcohol are added to MeCN rich mixtures,  $\beta_{\text{NH}_2}$  shows an almost linear behavior in contrast with the observed for  $\beta_{\text{OH}}$ . This trend confirms what was previously noticed by Laurence and Nicolet [32,37]. According to these authors “at least a significant part of the difference in the HB ranking defined by  $\beta_{\text{OH}}$  and



**Fig. 5.** Variation of the average Kamlet–Taft parameters as a function of composition in the studied ternary solvent mixture, at 298.15 K. The represented surfaces result from a polynomial fitting function.

$\beta_{\text{NH}_2}$  originates in the fact that indicator D has two acidic hydrogens". Moreover, the behavior herein evidenced can also be a result of family dependence, which was also anticipated by the same authors, as well as by Abboud and Notario [44] in their compilation of scales of solvent polarity.

Fig. 5b presents  $\beta$  values for the ternary mole fractions which also result from an arithmetic average, in this case of the two  $\beta$  scales,  $\beta_{\text{NH}_2}$  and  $\beta_{\text{OH}}$ . The behavior in the ternary mixture composition regions can again be mainly explained by the binary contributions, being the "ternary influence" clearly residual and within the experimental uncertainty associated in each region to the corresponding binary input.

The analysis of  $\alpha_{\text{OMe}}$  based on the pair 4-nitroanisole/betaine (30) (Fig. 4e) shows the following trends: MeOH/1-PrOH mixture depicts an approximately ideal behavior with a minor negative deviation. Mixtures with MeCN exhibit strong deviations from ideality, with maximum positive synergism for mole fractions between 0.7 and 0.8 in MeCN. As regards the  $\alpha_{\text{NMe}_2}$  parameter (Fig. 4f) in MeOH/1-PrOH the behavior is once more nearly ideal, whereas in 1-PrOH/MeCN and MeOH/MeCN sharp positive deviations are observed as before, with maximum departures from ideality at mole fractions between 0.7 and 0.8 in MeCN. Interestingly, in MeCN mixtures, the addition of small amounts of the other component causes their acidity, measured by  $\alpha$ , to increase abruptly.

Fig. 5c displays the variation of  $\alpha$  with composition in the ternary environment. Again, average values resulting from the two  $\alpha_{\text{OMe}}$  and  $\alpha_{\text{NMe}_2}$  scales are shown. The observed behavior can be mostly explained, within experimental uncertainty, by the binary contributions.

It is important to mention why in the context of this work the solvation models have not been applied to solvatochromic parameters. The reason is conceptual: if solvation models intend to mimic the solvation of a given probe in a certain solvent system, then microscopic parameters, in particular  $\alpha$  and  $\beta$ , which reflect the behavior of more than one probe, would result in solvation parameters with questionable meaning.

Comparing the solvatochromic parameters for the pure solvents obtained in this study with published values [40], some differences are readily observed but, in general, they are not very significant ( $\leq 10\%$ ). The exceptions are  $\alpha$  and  $\pi^*$  values for MeCN ( $>14\%$ ). This finding is, however, not critical for the present analysis. The explanation for these differences may lie on the fact that these parameters might have been obtained by different probes and/or experimental methods than those used in the literature; or, possibly, literature values might have been incorrectly determined in acetonitrile (Table 2).

## Conclusions

The behavior of  $\alpha$ ,  $\beta$ , and  $\pi^*$  in MeOH/1-PrOH was, as expected, and given the chemical nature of the two components, close to ideality, and whenever some deviations arise they are usually not very significant.

The addition of small amounts of MeCN to the binary mixtures containing alcohol, leads to an increase in  $\pi^*$ , above the expected

for an ideal behavior, particularly for 1-PrOH/MeCN. This non-specific enhanced capacity of charge solvation seems to occur by the action of MeCN, a very polar and polarizable molecule.

On the other hand, there is a high correlation between the wavenumbers for the indicators that define parameters  $\pi_{\text{NMe}_2}^*$  and  $\pi_{\text{OMe}}^*$ , and thus, as anticipated, the behavior of these parameters is also very similar throughout the whole solvent composition range.

The same does not hold for the  $\beta_{\text{OH}}$  and  $\beta_{\text{NH}_2}$  scales where, despite a reasonable correlation between the wavenumber values for the two indicators that define the two scales, substantially different variations with composition are observed. This is particularly noticeable in MeOH/MeCN and 1-PrOH/MeCN, with deviations from ideality in opposite directions. This trend can be explained by the different basic character of the probes  $-\text{OH}$  and  $-\text{NH}_2$  groups. For MeOH/MeCN and 1-PrOH/MeCN, the addition of the alcohol component to MeCN leads to a rapid increase in Lewis basicity in terms of  $\beta_{\text{OH}}$  as a result of the possibility of interaction between the solvent and the  $-\text{OH}$  group of the probe. Conversely, in terms of  $\beta_{\text{NH}_2}$ , the addition of MeCN to pure alcohols leads to a decrease in Lewis basicity, greater than that expected if an ideal behavior was to be perceived, as a consequence of the interaction of the solvent with the  $-\text{NH}_2$  group of the probe.

The acidity scales  $\alpha_{\text{OMe}}$  and  $\alpha_{\text{NMe}_2}$  do not reveal large differences between them. Yet, the two scales show in MeCN rich regions, a sharp increase in acidity by the addition of small amounts of any of the other components, either 1-PrOH or MeOH. This behavior suggests that the incorporation of MeCN in the mixture destroys part of the pre-existing solvent/solvent (in this case, alcohol/alcohol) interactions. Co-solvent molecules become, therefore, more available to interact with the solvatochromic probes through hydrogen bonding. This is why positive deviations to ideality are detected in  $\alpha$ , for MeCN rich regions. However, this behavior should also result in an increase in the molar volume of the mixtures which does not happen for the mixture MeOH/MeCN [23]. This can be rationalized in terms of the creation of new and stronger solvent/solvent heteromolecular interactions between methanol and acetonitrile.

The behavior of  $\alpha$ ,  $\beta$ , and  $\pi^*$  in the ternary mole fractions regions results largely from the sum of the binary contributions, and the possible ternary inputs are always negligible, being, in each composition region, within the experimental uncertainty associated with the corresponding values obtained for the binary mixtures.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.01.021>.

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**Table 2**  
Parameter comparison for the pure solvents [40].

	MeOH	1-PrOH	MeCN
$\pi_{\text{average}}^*$	0.66	0.57	0.75
$\pi_{\text{literature}}^*$	0.60	0.52	0.66
$\beta_{\text{average}}$	0.67	0.84	0.36
$\beta_{\text{literature}}$	0.66	0.90	0.40
$\alpha_{\text{average}}$	0.99	0.77	0.34
$\alpha_{\text{literature}}$	0.98	0.84	0.19

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