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Grouping of hydrogen-bond ability of pure solvents and their binary mixtures based on the similarity of their microscopic properties. Part 2

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The work presents a *grouping scheme* of some pure solvents (which are able to form hydrogen-bonded complexes) and their binary mixtures on the basis of the similarity of their molecular-microscopic properties. The solvatochromic parameters SPP, SA, and SB developed by Catalán *et al*. are selected as clustering variables. The Ward Method (WM) and the Group Average Method (GA) are applied as clustering procedures. The study pays particular attention to the microscopic solvent feature common to all solvents included in each cluster, describing the relevant solvating properties. It also contributes to a better understanding of the similarities and differences of the explored solvents.

Supporting information may be found in the online version of this article.

Keywords: molecular-microscopic solvent properties; solvatochromic parameters; binary mixtures; multiparametric approaches; linear correlation; multivariate methods (cluster analysis)

INTRODUCTION

The active role of solvents in chemical processes has long been recognized. From the combination of pure solvents in binary mixtures, both the availability and diversity of reaction mediums have strongly increased. Different empirical scales have been proposed for describing the solvation interactions at a molecular level.[1] Among them, one of the most extensively used method is the one based on the use of solvatochromic reference probes reflecting the specific and non-specific solute–solvent interactions and their influence on the UV–Vis spectral band shifts. The multiparametric approaches particularly associate each kind of solute–solvent interaction with a separate parameter. All parameters are necessary to reflect the overall solvation power of the solvent. In this direction, π^*, β, and α scales have been developed by Kamlet, Abboud, and Taft (KAT)[2–4] with the purpose of quantifying the dipolarity/polarizability, hydrogen-bond basicity and hydrogen-bond acidity of the solvent, respectively. More recently, Catalán and co-workers[5–9] have analogously defined the SPP dipolarity/polarizability, SB basicity and SA acidity scales. It should be remarked that both the KAT and the Catalán approaches are based on the application of the solvatochromic comparison method,[2–4] the reference solutes proposed to construct each scale being quite different.

The chemical characteristics of mixed solvents are customarily determined by the same techniques applied to pure solvents. However, solute–solvent interactions are more complex in mixed solvents than in pure solvents owing to the intermolecular solvent–solvent interactions and to the preferential solvation phenomenon.[10] A recent investigation showed that binary mixtures can be characterized with the same accuracy as pure solvents in terms of SPP, SB, and SA scales although the preferential solvation is influenced by features of the solute such as its shape, charge, properties, and size.[11] Previous studies reported by our group[12–16] include the determination of the empirical parameters π^*, β, and α for binary solvent mixtures mainly formed by aprotic solvents, in which specific intersolvent interactions are involved. In this direction we have analyzed the preferential solvation effects for the reference solutes used in the quantification of the KAT parameters through the application of preferential solvation models; the response patterns of the solvent mixtures to the chemical properties of the probes; the correlation between the solvent parameters and the data corresponding to other solvent-dependent processes (kinetic results of aromatic nucleophilic substitution reactions); the convergence for KAT parameter values obtained from comparable solutes; and a grouping scheme of some pure solvents and their binary mixtures on the basis of the similarity of their molecular-microscopic properties, with solvatochromic parameters π^*, α, and β of KAT.

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More recently we presented the molecular-microscopic characterization of 10 binary solvent mixtures based on solvatochromic reference solutes by a comparison of multiparametric empirical solvent scales: π^*, α, and β and SPP, SA, and SB. The results obtained, by the Bland and Altman method, provided good evidence of the fact that the scales involved are dependent on the type of probes and method used to develop each scale. Even though both multiparametric approaches are rather powerful tools to quantify the molecular-microscopic solvent properties of pure and mixed solvents, the correct measurements remain unknown.[17]

At this point, our attention was drawn to group the same 10 binary solvent mixtures by the multivariate methods of cluster analysis, using the solvatochromic parameters SPP, SA, and SB, as clustering variables. In this direction, the aim of the present work is threefold: (i) to analyze analogies and differences of separate groups of solvents in terms of nature and strength of their microscopic properties represented by SPP, SA, and SB, (ii) to compare with the grouping scheme previously obtained with the KAT scales, and (iii) to describe the general features of the grouped mixed solvents in order to contribute with an appropriate media selection and, in conjunction with linear solvation energy relationships (LSER), to predict the solvent effects on a chemical process.

RESULTS AND DISCUSSION

The solvent systems involved in this analysis are considered representative of different types of binary mixtures in which the pure components are able to form complexes or cross-associated species via hydrogen bonding between them. Moreover, it can be pointed out that the molecular associates are believed to be relevant to the behavior of the mixtures.[15,18–22]

The pure solvents which take part in the selected mixtures are ethyl acetate (EtAcO), dimethylsulfoxide (DMSO), acetonitrile (AcN), trichloromethane ($CHCl_3$), dichloromethane (CH_2Cl_2), and methanol (MeOH). Its properties are presented in Table 1.[2–9,11]

The solvent systems investigated are: [EtAcO + cosolvent $CHCl_3$ or AcN or MeOH], [DMSO + cosolvent $CHCl_3$ or CH_2Cl_2 or AcN or MeOH], [AcN + cosolvent $CHCl_3$ or MeOH], and [$CHCl_3$ + MeOH].

Table 1. The properties SPP, SB, and SA of the pure solvents which take part in the selected mixtures

	Parameters					
Solvents	π^*	α	β	SPP	SA	SB
EtAcO	0.55	0	0.45	0.795	0	0.542
DMSO	1	0	0.76	1	0.072	0.647
AcN	0.75	0.19	0.40	0.895	0.044	0.286
$CHCl_3$	0.58	0	0.10	0.876	0.040	0.178
CH_2Cl_2	0.82	0.13	0.10	0.786	0.047	0.071
MeOH	0.60	0.98	0.66	0.857	0.605	0.545

References[2–9,11] and references cited therein.

An analysis of analogies and differences of separate groups of solvents in terms of SPP, SA, and SB

Clustering procedures

Two clustering methods have been employed: the Ward Method (WM) and the Group Average Method (GA). They present different mathematical backgrounds.

Both the WM and the GA are hierarchical methods. In hierarchical methods, each observation begins in its own cluster. Two clusters are then merged to form a new cluster that replaces two old clusters. This process is repeated until only one cluster is left, or until a reasonable value for the number of clusters is obtained, looking at the corresponding dendogram (in which the members are grouped according to their similarity). WM is a procedure that calculates the distance between two clusters as the sum of squares between the two clusters summed over all the variables. GA is a procedure that calculates the distance between two clusters as the average distance from observations in one cluster to observation in another cluster. For the selected variables, the principal component analysis is not necessary given both the three-dimensional character of the raw data and their proven non-significant correlation. The clustering techniques have been applied as implemented in the Statgraphics Plus Version 7.1. The Euclidean distance has been adopted as the similarity measurement. (A brief summary of the statistical methodology is presented in the Supporting Information.)

Figures 1 and 2 show the dendograms corresponding to the WM and the GA. Figures 3 and 4 show the cluster scatterplots for the WM and the GA, respectively. The relevant information is collected in Table 2. The pure solvents and the binary mixtures included in each cluster are presented in Tables 3 and 4, for WM and GA, respectively.

As can be seen from the comparison of the obtained data, the application of both techniques of clustering generates similar results. Both the WM and the GA tend to give similar sized clusters with more similitude of cluster central coordinates.

Cluster 1: Both methods include the same pure solvents in this group: EtAcO, AcN, $CHCl_3$, and CH_2Cl_2, which are dipolar/polarizable solvents with HBA or HBD capability (AcN exhibits both hydrogen bonding properties simultaneously) and their mixtures (EtAcO + $CHCl_3$ or AcN) and (AcN + $CHCl_3$), in all cases at nine cosolvent molar fractions. This cluster also includes molar fractions corresponding to the mixtures of the highly dipolar/polarizable and strong HBA solvent (DMSO with $CHCl_3$ or CH_2Cl_2 or AcN) at the highest cosolvent concentrations. Finally, this cluster includes the ($CHCl_3$ + MeOH) and (EtAcO + MeOH) mixtures corresponding to low cosolvent concentrations. For these latter mixtures, we observe small differences between both

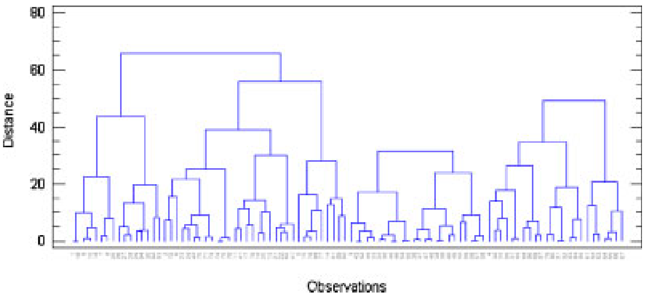

Figure 1. Dendogram obtained according to Ward Method, Euclidean distance

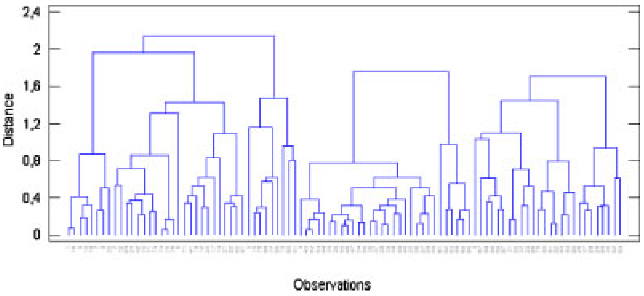

Figure 2. Dendogram obtained according to Group Average Method, Euclidean distance

methods: (WM includes the following cosolvent molar fractions $x = 0.1$–0.7 and $x = 0.1$–0.6 for these mixtures, respectively. GA includes the following cosolvent molar fractions $x = 0.1$ and $x = 0.1$–0.4 for these mixtures, respectively).

From the SPP, SA, and SB values and according to the cluster central coordinates (Table 2), the dipolarity/polarizability appears to be the determinant property. On the other hand, the HBA ability should play a greater significance than that related to the HBD ability.

Cluster 2: Both methods include DMSO as pure solvent, and contain binary mixtures of (DMSO with $CHCl_3$, or CH_2CH_2 or AcN) in identical cosolvent molar fractions: $x = 0.1$–0.7, $x = 0.1$–0.8, and $x = 0.1$–0.8, respectively. With respect to system (DMSO + MeOH), the differences observed due to the application of both clustering techniques is that GA includes cosolvent molar fractions: $x = 0.1$–0.6. While that this system disappears for the WM.

The solvent parameters and the cluster central coordinates show that, as in *Cluster 1*, the dipolarity/polarizability is the determinant property. Moreover, the HBA ability is also a strong differentiating factor among solvent mixtures.

Cluster 3: This group contains pure solvent MeOH. Agreement in the results obtained from the application of both methods is observed, for the (AcN + MeOH) system, at nine cosolvent molar fractions. While small differences are presented for systems (EtAcO + MeOH), and ($CHCl_3$ + MeOH), [$x = 0.7$–0.9 in WM and 0.2–0.9 in GA for system (EtAcO + MeOH) and $x = 0.8$–0.9 in WM and 0.5–0.9 in GA for system ($CHCl_3$ + MeOH)]. The most important difference is in the (DMSO + MeOH) system. In this case, the WM method includes the nine cosolvent molar fractions while the GA method only includes $x = 0.7$–0.9. This is the zone dominated by the cosolvent.

The solvent parameters SPP, SA, and SB and the cluster central coordinates reveal that the HBD character plays the most relevant role.

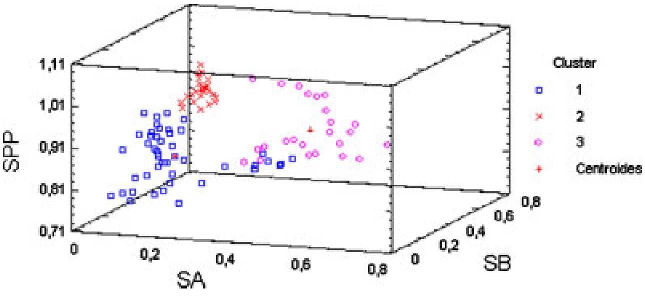

Figure 3. Cluster scatterplot obtained according to Ward Method, Euclidean distance

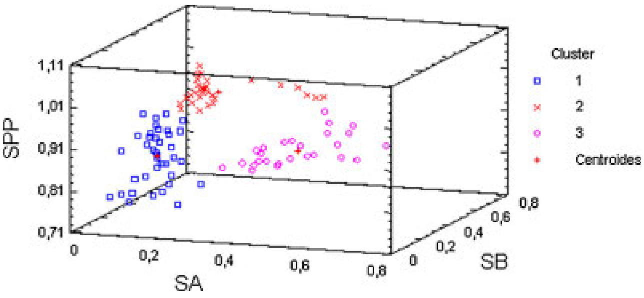

Figure 4. Cluster scatterplot obtained according to Group Average Method, Euclidean distance

Solvent feature of the mixtures included in each cluster

The solvent feature includes the overall ability of interactions related to all the molecular-microscopic properties. The most remarkable characteristic common to each group can be evaluated from the central coordinates values.

The dipolarity/polarizability appears to be the most discriminating parameter in *Clusters 1 and 2*. The solvents included in these clusters can develop non-specific molecular interactions with solutes. The cause of splitting between both groups of solvents can be attributed to the intensity of the cited property. Nevertheless, the specific interactions (particularly the HBA basicity) also play a role. On the other hand, the remarkable characteristic of the members included in *Cluster 3* is the capacity to develop specific interactions acting as HBD solvents.

We can conclude that (i) the mixtures which take part in *Cluster 1* are poorly acidic, moderately basic, dipolar/polarizable solvents; (ii) the mixtures included in *Cluster 2* are strong dipolar/polarizable solvents with high HBA ability and scarce HBD capacity; and (iii) the mixtures corresponding to *Cluster 3* are strong HBD dipolar/polarizable solvents, with HBA ability. It can also be remarked that some solvent systems show changes in clustering with the mixtures composition, the intersolvent complexes being relevant to the behavior of the mixtures.

These results contribute to our understanding of the differences in the chemical nature of these solvent systems, providing information about the molecular interactions which can be established with solute molecules.

Comparison of the grouping scheme obtained in the present work with the grouping scheme previously obtained with the KAT scales: analogies and differences

The Ward Method

Cluster 1: Both groupings include the same pure solvents: EtAcO, AcN, $CHCl_3$, and CH_2Cl_2, and their binary mixtures (EtAcO + $CHCl_3$ or AcN), (AcN + $CHCl_3$), in all cases at nine cosolvent molar fractions. Additionally, they include ($CHCl_3$ + MeOH) mixtures at very similar cosolvent concentrations (grouping with KAT parameters $x = 0.1$–0.5, while with Catalán parameters $x = 0.1$–0.7).

The most substantial difference was observed in the (EtAcO + MeOH) system. In this case, the mixtures corresponding to the range ($x = 0.1$–0.6) cosolvent concentrations were grouped for the Catalán parameters; however, this system was totally included in *Cluster 3* for the KAT parameters (dominated by MeOH).

Table 2. Cluster information according to the results obtained through the Ward Method (WM) and Group Average Method (GA)

				Cluster central coordinates		
Method	Cluster	Members	Percent	SPP	SA	SB
WM	1	48	50.00	818	085	433
	2	24	25.00	939	077	639
	3	24	25.00	0.885	0.405	0.530
GA	1	40	41.67	0.823	0.049	0.405
	2	30	31.25	0.944	0.130	0.635
	3	26	27.08	838	379	523

Cluster 2: Both groupings include DMSO as pure solvent, and contain binary mixtures of (DMSO with $CHCl_3$, or CH_2CH_2 or AcN) cosolvents at very similar cosolvent concentrations. With respect to system (DMSO + MeOH), the difference observed is that the grouping with KAT parameters includes the following cosolvent molar fractions: $x = 0.1$–0.3 (i.e., the zone dominated by DMSO) while this system disappears in the grouping whit the Catalán parameters.

Cluster 3: Both groupings contain the pure solvent MeOH. Agreement in the results obtained is observed for the (AcN + MeOH) system, at the nine cosolvent molar fractions while a small difference is presented for the ($CHCl_3$ + MeOH) system, ($x = 0.8$–0.9 in grouping with the Catalán parameters and 0.6–0.9 for the KAT parameters). The most important differences are in systems: (EtAcO + MeOH) and (DMSO + MeOH). In the first case, this system is totally included in this cluster for the KAT parameters, while the grouping with the Catalán parameters only includes the rich zone in cosolvent ($x = 0.7$–0.9). In the second case, the grouping with Catalán parameters includes the nine cosolvent molar fractions and the grouping with KAT parameters only $x = 0.4$–0.9. This is the zone dominated by the cosolvent.

The group average

Cluster 1: Both groupings include the same pure solvents: EtAcO, AcN, $CHCl_3$, and CH_2Cl_2, and their binary mixtures (EtAcO + $CHCl_3$ or AcN) and (AcN + $CHCl_3$), in all cases at nine cosolvent molar fractions. Additionally, they include ($CHCl_3$ + MeOH) mixtures at very similar low cosolvent concentrations (grouping with KAT parameters $x = 0.1$–0.5, and grouping with Catalán parameters $x = 0.1$–0.4). An identical composition for system (DMSO + AcN) [$x = 0.9$] is included in both groupings. A small difference is presented by the (DMSO + $CHCl_3$) system: ($x = 0.8$–0.9 for grouping by Catalán parameters, and $x = 0.6$–0.9 for grouping by KAT parameters).

Cluster 2: Both groupings include DMSO as pure solvent, and contain binary mixtures of (DMSO + AcN or MeOH) in identical composition. Additionally, they include (DMSO + $CHCl_3$ or CH_2CH_2) mixtures at very similar cosolvent concentrations. In the first case, for the grouping with Catalán parameters $x = 0.1$–0.7 and for the grouping with KAT parameters $x = 0.1$–0.5. In the second case, for the grouping with Catalán parameters $x = 0.1$–0.8 and for the grouping with KAT parameters $x = 0.1$–0.9.

Cluster 3: Both groupings contain the pure solvent MeOH. Agreement in the results obtained is observed for the (AcN + MeOH) and (DMSO + MeOH) systems, at the nine cosolvent molar fractions while small differences are presented for the ($CHCl_3$ + MeOH) and (EtAcO + MeOH) systems, and consequently with the different grouping in *Cluster 1*. In the first case, $x = 0.5$–0.9 in grouping with the Catalán parameters and 0.6–0.9 for the KAT parameters. For system (EtAcO + MeOH), $x = 0.2$–0.9 in grouping with the Catalán parameters and the nine cosolvent molar fractions with KAT parameters.

Although the compared scales are dependent of the probe type and of the method used to develop them, these substantial ones differ they would not reflect in the clustering.

Table 3. Clusters obtained through the application of the Ward Method

Pure solvents	Solvent mixtures			
		Cluster 1		
EtAcO, AcN, $CHCl_3$, CH_2Cl_2	EtAcO + $CHCl_3$ $X_{CoS} = 0.1$–0.9	EtAcO + AcN $X_{CoS} = 0.1$–0.9	EtAcO + MeOH $X_{CoS} = 0.1$–0.6	$CHCl_3$ + MeOH $X_{CoS} = 0.1$–0.7
	AcN + $CHCl_3$ $X_{CoS} = 0.1$–0.9	DMSO + $CHCl_3$ $X_{CoS} = 0.8$–0.9	DMSO + CH_2Cl_2 $X_{CoS} = 0.9$	DMSO + AcN $X_{CoS} = 0.9$
		Cluster 2		
DMSO	DMSO + $CHCl_3$ $X_{CoS} = 0.1$–0.7	DMSO + CH_2Cl_2 $X_{CoS} = 0.1$–0.8	DMSO + AcN $X_{CoS} = 0.1$–0.8	
		Cluster 3		
MeOH	EtAcO + MeOH $X_{CoS} = 0.7$–0.9	DMSO + MeOH $X_{CoS} = 0.1$–0.9	AcN + MeOH $X_{CoS} = 0.1$–0.9	$CHCl_3$ + MeOH $X_{CoS} = 0.8$–0.9

Table 4. Clusters obtained through the application of the Group Average Method

Pure solvents	Solvent mixtures			
		Cluster 1		
EtAcO, AcN, $CHCl_3$, CH_2Cl_2	EtAcO + $CHCl_3$ $X_{CoS} = 0.1–0.9$	EtAcO + AcN $X_{CoS} = 0.1–0.9$	EtAcO + MeOH $X_{CoS} = 0.1$	$CHCl_3$ + MeOH $X_{CoS} = 0.1–0.4$
	AcN + $CHCl_3$ $X_{CoS} = 0.1–0.9$	DMSO + $CHCl_3$ $X_{CoS} = 0.8–0.9$	DMSO + CH_2Cl_2 $X_{CoS} = 0.9$	DMSO + AcN $X_{CoS} = 0.9$
		Cluster 2		
DMSO	DMSO + $CHCl_3$ $X_{CoS} = 0.1–0.7$	DMSO + CH_2Cl_2 $X_{CoS} = 0.1–0.8$	DMSO + AcN $X_{CoS} = 0.1–0.8$	DMSO + MeOH $X_{CoS} = 0.1–0.6$
		Cluster 3		
MeOH	EtAcO + MeOH $X_{CoS} = 0.2–0.9$	DMSO + MeOH $X_{CoS} = 0.7–0.9$	AcN + MeOH $X_{CoS} = 0.1–0.9$	$CHCl_3$ + MeOH $X_{CoS} = 0.5–0.9$

Application

The usual linear correlation between empirical solvent parameters and other solvent-dependent properties (e.g., logarithms of rate and equilibrium constants, absorption energies) can be considered as manifestations of general LSER.[23–25] In earlier papers, we analyzed the correlation between the microscopic solvent properties of pure and mixed solvents with the kinetic data for aromatic nucleophilic substitution (S_NAr) reactions performed in those solvents, in order to interpret the solvent effects on the reaction rate.[12–16] The strong influence of the solvent on the rate of the S_NAr reactions between halonitrobenzenes and amines is well known. In this direction, different systematic studies have been reported not only in pure solvents but also in a substantial number of binary mixtures.[26–28]

Now, the interest is to relate the microscopic characteristics of solvents merged together in each cluster proposed here with previously reported kinetic data corresponding to a S_NAr reaction, in order to gain a greater understanding on the prediction of solvent effects on the chemical reaction.

LSER. We selected the reported kinetic results[12–16,26,29,30] corresponding to the reaction of 2,4-dinitrochlorobenzene (2,4-DNCB) with piperidine (PIP) carried out in pure solvents and in some binary mixtures particularly chosen corresponding to Clusters 1 and 3 (grouped by the application of the WM) in order to perform a correlation analysis. Unfortunately, we did not find an acceptable correlation of the kinetic data of this reaction with the parameters of the system of solvents corresponding to Cluster 2 ($r = 0.892$, with data number 14), perhaps as a result of the HBA ability, factor that differs strongly from this cluster. Nevertheless, in this cluster we found a good correlation for the kinetic results corresponding to the reaction of 2,4-dinitrofluorobenzene (2,4-DNFB) with butylamine (BU) carried out in pure solvents and in some binary mixtures particularly selected also grouped by the application of the WM.

For these reactions, a two-step mechanism was established, the formation of the intermediate being the rate-determining step.

The correlation between the logarithm of the rate constant with the molecular-microscopic solvent properties was analyzed according to the model: $\log k_A = Y + s\mathrm{SPP} + a\mathrm{SA} + b\mathrm{SB}$. The results are presented in Table 5. The regression equation was assessed by the evaluation of the correlation coefficient and the standard deviation revealing that there is acceptable correspondence between the reaction rate and the solvent properties. These results allow us to make predictions regarding the influence of the media on the rate of the selected reaction. They particularly demonstrate the excellent correlation obtained in Cluster 3 (refer Table 5) formed by mixtures with similar properties even though constituted by pure solvents of different nature.

Table 5. Correlation analysis data: correlation coefficient (*r*), standard deviation (SD), intercept (*Y*), parameters *s*, *a*, and *b* (and their standard errors), and number of data points (*n*)

$\log k_A = Y + s\mathrm{SPP} + a\mathrm{SA} + b\mathrm{SB}$	Cluster 1	Cluster 2	Cluster 3
	EtAcO; $CHCl_3$, EtAcO + $CHCl_3$ $X_{CoS} = 0.1–0.9$, $CHCl_3$ + MeOH $X_{CoS} = 0.1–0.4$	DMSO, DMSO + $CHCl_3$ $X_{CoS} = 0.1–0.7$	MeOH, EtAcO + MeOH $X_{CoS} = 0.7–0.9$, $CHCl_3$ + MeOH $X_{CoS} = 0.8–0.9$ DMSO + MeOH $X_{CoS} = 0.1–0.9$
r (r^2)	0.979 (0.959)	0.977 (0.956)	993 (0.986)
SD	092	089	105
Y (S_Y)	−2.122(0.398)	−6.970 (2.982)	−10.63 (1.170)
s (S_s)	−1.106 (0.494	10.14 (1.125)	8.741 (0.740)
a (S_a)	−5.489(0.420)	20.25 (4.812)	−1.553 (0.570)
b (S_b)	255(0.165)	−3.994 (4.78)	4.175 (2.056)
n	15	8	15

CONCLUSIONS

First, from the analogies and differences of the obtained groups of solvents, we can conclude that the division is clear as a function of the dipolarity/polarizability, acidity and basicity dominating each group in terms of nature and strength of their microscopic properties represented by SPP, SA, and SB. Second, both systems of scales (KAT and Catalán) lead identical groupings of these pure solvents and their mixtures despite the different nature of the tests and their previous lack of agreement.[17] The similarities in the grouping of the systems of research solvents are much more noteworthy and important than the differences. Finally, *LSER* represented by a model such as: $\log k_A = Y + s\text{SPP} + a\text{SA} + b\text{SB}$, allow us to make predictions regarding the influence of the media on the rate of the selected reactions.

EXPERIMENTAL

For the proposed mixtures, the SPP, SB, and SA empirical parameters are available at nine molar fractions of cosolvent[17,31,32] and are presented in Supporting Information: Tables VI, (EtAcO + cosolvent: $CHCl_3$ or AcN or MeOH), VII (DMSO + cosolvent: $CHCl_3$ or CH_2Cl_2 or AcN or MeOH), and VIII (AcN + cosolvent: $CHCl_3$ or MeOH, and $CHCl_3$ + MeOH).

The original data matrix to be clustered is made up of 96 solvents: six pure solvents, in the following order: EtAcO, AcN, DMSO, MeOH, CH_2Cl_2, $CHCl_3$ (numbers: 1–6), and their selected binary mixtures, which are considered at nine molar fractions of cosolvent in each case, in the following order: EtAcO + $CHCl_3$ (numbers: 7–15); EtAcO + AcN (numbers: 16–24); EtAcO + MeOH (numbers: 25–33); DMSO + $CHCl_3$ (numbers: 34–42); DMSO + CH_2Cl_2 (numbers: 43–51); DMSO + AcN (numbers: 52–60); DMSO + MeOH (61–69), AcN + $CHCl_3$ (numbers: 70–78): AcN + MeOH (numbers: 79–87); $CHCl_3$ + MeOH (88–96). These numbers of order corresponding to *x*-axes of the dendograms showed in Figs. 1 and 2).

The kinetic data corresponding to reactions [2,4-DNCB + PIP] carried out in solvent system corresponding to Clusters 1 and 3 are presented in Table IX, and the data of [2,4-DNFB + BU] carried out in solvent system corresponding to Cluster 2 are presented in Table X in Supporting Information.

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