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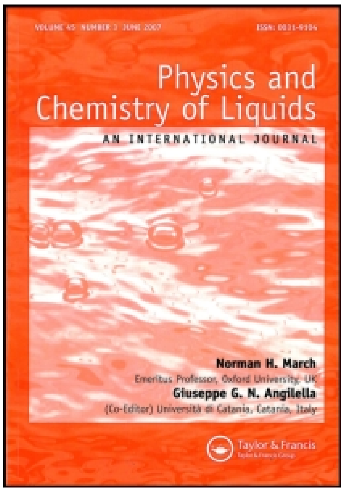

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Grouping of Hydrogen-Bond Ability of Pure Solvents and their Binary Mixtures Based on the Similarity of their Microscopic Properties

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GROUPING OF HYDROGEN-BOND ABILITY OF PURE SOLVENTS AND THEIR BINARY MIXTURES BASED ON THE SIMILARITY OF THEIR MICROSCOPIC PROPERTIES

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This 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 π^*, α and β developed by Kamlet, Abbound and Taft, are selected as clustering variables. The Ward's Method and the Group Average Method 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. In addition, the correspondence between reaction rates and solvent chemical properties is evaluated through the application of linear solvation energy relationships.

Keywords: Solvent mixtures; Molecular–microscopic properties; Solvatochromic solvent parameters

INTRODUCTION

The active role of solvents in chemical processes has long been recognized. The behavior of a solvent can be investigated by means of solvatochromic reference solutes considered as chemical probes, which reflect the specific and nonspecific solute–solvent interactions on the UV–Visible spectral shifts. In this direction, a number of empirical solvatochromic parameters have been proposed to quantify the molecular–microscopic solvent properties [1]. Among them, the Kamlet, Abboud and Taft multiparametric approach attempts at separating dipole–dipole and polarizability effects from hydrogen-bonding effects by means of the π^* scale of dipolarity/polarizability, the α scale of the hydrogen-bond donor acidity, and the β scale of hydrogen-bond basicity [2].

A classification of 42 pure solvents based on π^*, α and β solvatochromic parameters selected as microscopic solvent descriptors has recently been reported according to the results obtained from the application of several multivariate clustering techniques. The

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solvent classification scheme is presented as a tool to be applied in the solvent selection [3]. The possibility of using mixed solvents provides a useful extension of the range of solvents available.

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 solvent–solvent interactions and to the preferential solvation phenomenon [4]. We have recently characterized several nonaqueous binary mixtures of solvents where both pure components are able to form complexes or cross-associated species by hydrogen-bonding, on the basis of the solvatochromism of a set of reference solutes [5]. In this connection, the present work is focused on to group solvent mixtures of the cited types according to similarity in molecular–microscopic properties, through the application of multivariate clustering techniques, in order to avoid biased criteria from the chemist in the solvent-grouping. The solvatochromic parameters π^*, α and β are selected as clustering variables. The aims are: (i) to analyze analogies and differences of separate groups of solvents in terms of nature and strength of their microscopic properties; and (ii) 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

Four kinds of binary mixtures were selected for this analysis: A [hydrogen bond acceptor (HBA) solvent + hydrogen bond donor (HBD) cosolvent]; B [HBA/HBD solvent + HBD cosolvent]; C [HBA solvent + HBA/HBD cosolvent] and D [HBA/HBD solvent + HBA/HBD cosolvent]. It can be pointed out that the molecular associates are believed to be relevant to the behavior of the mixtures [6–8].

Experimental data The selected solvents which make up the mixtures are: ethyl acetate (EtAcO, $\pi^* = 0.55$, $\alpha = 0.00$, $\beta = 0.45$) and dimethylsulfoxide (DMSO, $\pi^* = 1.00$, $\alpha = 0.00$, $\beta = 0.76$) as aprotic HBA solvents, chloroform ($\pi^* = 0.58$, $\alpha = 0.20$, $\beta = 0.10$) and dichloromethane ($\pi^* = 0.82$, $\alpha = 0.13$, $\beta = 0.10$) as aprotic solvents with potential HBD ability, acetonitrile (AcN, $\pi^* = 0.75$, $\alpha = 0.19$, $\beta = 0.40$) as HBA/HBD aprotic solvent, and methanol (MeOH, $\pi^* = 0.60$, $\alpha = 0.98$, $\beta = 0.66$) as HBA/HBD protic solvent [5c]. The binary mixtures included in the analysis are: (EtAcO or DMSO + $CHCl_3$ or CH_2Cl_2), (AcN or MeOH + $CHCl_3$ or CH_2Cl_2), (EtAcO or DMSO + AcN or MeOH), and (AcN + MeOH), which were taken as representative of A, B, C and D, respectively. For the proposed mixtures, the empirical parameters π^*, α and β are available at nine molar fractions of cosolvent [5], except for ($CHCl_3$ + MeOH), (AcN + MeOH) and (DMSO + MeOH) which are determined in this work [the π^* values are previously reported for (DMSO + MeOH) [9]]. The microscopic properties corresponding to the latter mixtures were calculated according to general expressions collected by Marcus [10]. The dipolarity/polarizability was determined from the wavenumbers of the UV-visible absorption maxima of the solvatochromic indicators *N*,*N*-diethyl-4-nitroaniline (I) and 4-nitroanisol (II). The HBA ability was determined from the enhanced solvatochromic shifts for 4-nitroaniline (III) relative to (I). The HBA acidity was calculated from π^*, β and Dimroth–Reichardt ‘polarity’

TABLE I Experimental wavenumbers (in kK) and solvatochromic parameters for ($CHCl_3$ or AcN or DMSO + MeOH) solvent systems, measured at 25°C

		Cosolvent molar fractions								
Solvent	*Property*	*0.10*	*0.20*	*0.30*	*0.40*	*0.50*	*0.60*	*0.70*	*0.80*	*0.90*
$CHCl_3$ + MeOH	$\tilde{\nu}_{(I)}$	25.00	24.79	24.75	24.66	24.63	24.65	24.72	24.76	24.87
	$\pi^*_{(I)}$	0.79	0.86	0.87	0.90	0.91	0.90	0.88	0.87	0.83
	$\tilde{\nu}_{(II)}$	32.57	32.47	32.36	32.25	32.16	32.26	32.20	32.26	32.26
	$\pi^*_{(II)}$	0.66	0.70	0.75	0.80	0.84	0.79	0.82	0.79	0.79
	$\pi^*_{(avg)}$	0.73	0.78	0.81	0.85	0.87	0.85	0.85	0.83	0.81
	$\tilde{\nu}_{(III)}$	26.81	26.84	26.81	26.84	27.16	27.17	27.39	27.62	28.09
	β	0.67	0.65	0.62	0.57	0.43	0.45	0.37	0.31	0.16
	α^a	0.91	0.79	0.69	0.59	0.52	0.46	0.36	0.25	0.12
AcN + MeOH	$\tilde{\nu}_{(I)}$	25.00	25.00	24.96	24.94	24.94	24.94	25.00	25.00	25.12
	$\pi^*_{(I)}$	0.79	0.79	0.80	0.81	0.81	0.81	0.79	0.79	0.75
	$\tilde{\nu}_{(II)}$	32.46	32.46	32.46	32.39	32.46	32.46	32.46	32.57	32.57
	$\pi^*_{(II)}$	0.71	0.71	0.71	0.74	0.71	0.71	0.71	0.66	0.66
	$\pi^*_{(avg)}$	0.75	0.75	0.76	0.77	0.76	0.76	0.75	0.73	0.71
	$\beta^{(4)}$	0.53	0.54	0.55	0.56	0.57	0.59	0.61	0.63	0.65
	α^a	0.73	0.92	0.96	0.96	0.96	0.96	0.97	0.99	1.00
DMSO + MeOH	$\tilde{\nu}_{(III)}$	25.84	25.87	26.08	26.05	26.05	26.29	26.45	26.67	26.74
	β	0.76	0.75	0.74	0.74	0.76	0.70	0.70	0.68	0.67
	α^b	0.15	0.26	0.37	0.49	0.55	0.64	0.74	0.86	0.90

[a]Values calculated with $E_T(30)$ data from [4]; [b]Values calculated with $E_T(30)$ data from [16].

$E_T(30)$ values [4]. Table I presents the experimental UV–Visible absorption maximum of indicators I–III in ($CHCl_3$ or AcN or DMSO + MeOH) solvent systems, at nine mixture compositions. It also presents π^* values (which were calculated by the expressions $\pi^*_{(I)} = 0.314[27.52 - \sim_{(I)}]$ and $\pi^*_{(II)} = 0.427[34.12 - \sim_{(II)}]$), β values (which were calculated by $\beta = 0.358[31.10 - \sim_{(III)}] - 1.125\pi^*_{(I)}$), and α values (which were calculated by the previously reported $E_T(30)$ [5] and the expression $\alpha = 0.0692\ E_T(30) - 2.090 - 0.900\pi^* - 0.147\beta + 0.190\delta$).

1. *Clustering procedures* Two clustering methods have been employed: the Ward's Method (WM) and the Group Average Method (GA). They present different mathematical backgrounds.

The original data matrix to be clustered is made up of 114 solvents: 6 pure solvents and their selected binary mixtures (which are considered at nine molar fractions of cosolvent in each case).

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 nonsignificative correlation. The clustering techniques have been applied as implemented in the Statgraphics Plus Version 5.1. The Euclidean distance has been adopted as the similarity measurement.

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 II. The pure solvents and the binary mixtures included in each cluster are presented in Tables III and IV.

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 similarly sized clusters with identical 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 CH_2Cl_2 or AcN) and (AcN + $CHCl_3$ or CH_2Cl_2), in all cases at nine cosolvent molar fractions. This cluster also includes the ($CHCl_3$ + MeOH) mixtures corresponding to low cosolvent concentrations. The difference (five members) corresponds to the mixtures of the highly dipolar/polarizable and strong HBA solvent DMSO with $CHCl_3$ or AcN at high cosolvent concentrations, which are included only by the GA method. From the π^*, α, and β values [5] and according to the cluster central coordinates (Table II), the dipolarity/polarizability appears to be the determinant property ($0.56 \leq \pi^* \leq 0.87$). On the other hand, the HBA ability should play a greater significance than that related with the HBD ability.

Cluster 2 Both methods include DMSO as pure solvent. This group contains binary mixtures of DMSO with all the selected cosolvents. With respect to the systems DMSO + $CHCl_3$ or AcN, the differences observed due to the application of both clustering techniques involve the mixtures that the GA method includes in Cluster 1. On the other hand, both methods include MeOH-poor mixtures in Cluster 2 (the GA also incorporates $X_{\mathrm{MeOH}} = 0.4$–0.6 mixtures). The solvent parameters [5] and the cluster central coordinates show that, as in Cluster 1, the dipolarity/polarizability ($0.76 \leq \pi^* \leq 1.00$) is the determinant property. Moreover, the HBA ability is also a strong differentiating factor among solvent mixtures.

Cluster 3 This group contains the pure solvent MeOH. Their self-association and complex formation with EtAcO, DMSO, AcN and $CHCl_3$ are well known [6–8]. Agreement in the results obtained from the application of both methods is observed, excluding three mixtures with DMSO. The solvent parameters π^*, α, and β [5] and the cluster central coordinates reveal that the HBD character ($0.59 \leq \alpha \leq 1.00$) plays the relevant role.

On the other hand, the results show that the WM leads to grouping the mixtures with minor splitting among the members belonging to the same solvent system as the GA method. It also yields similarly sized subclusters (which is clearly observed in the dendograms, mainly for Clusters 1 and 2).

2. *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.

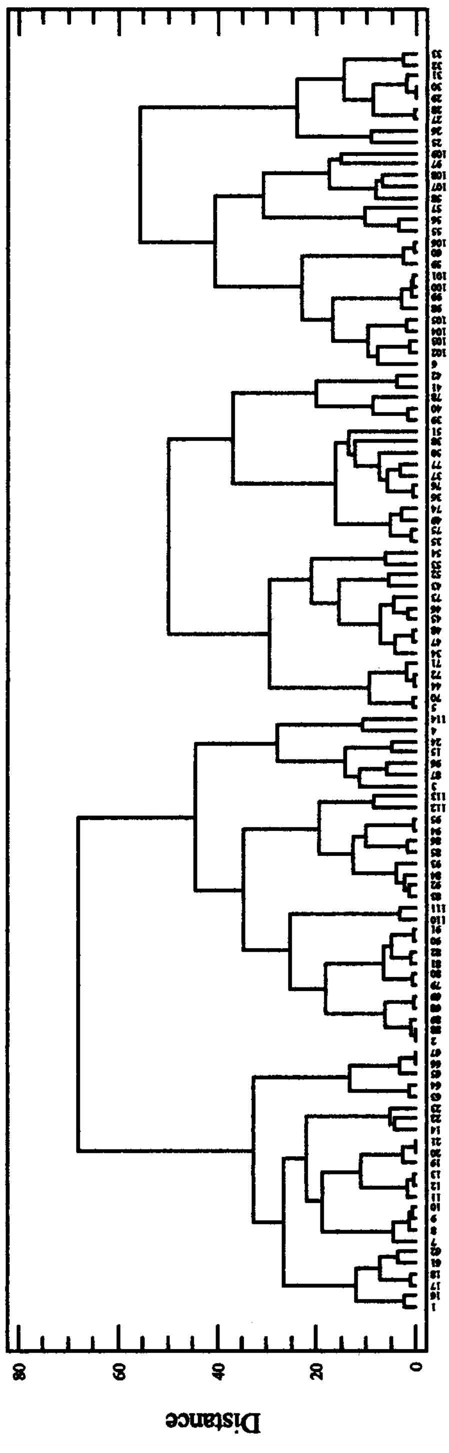

FIGURE 1 Dendogram obtained according to Ward's Method, Euclidean distance.

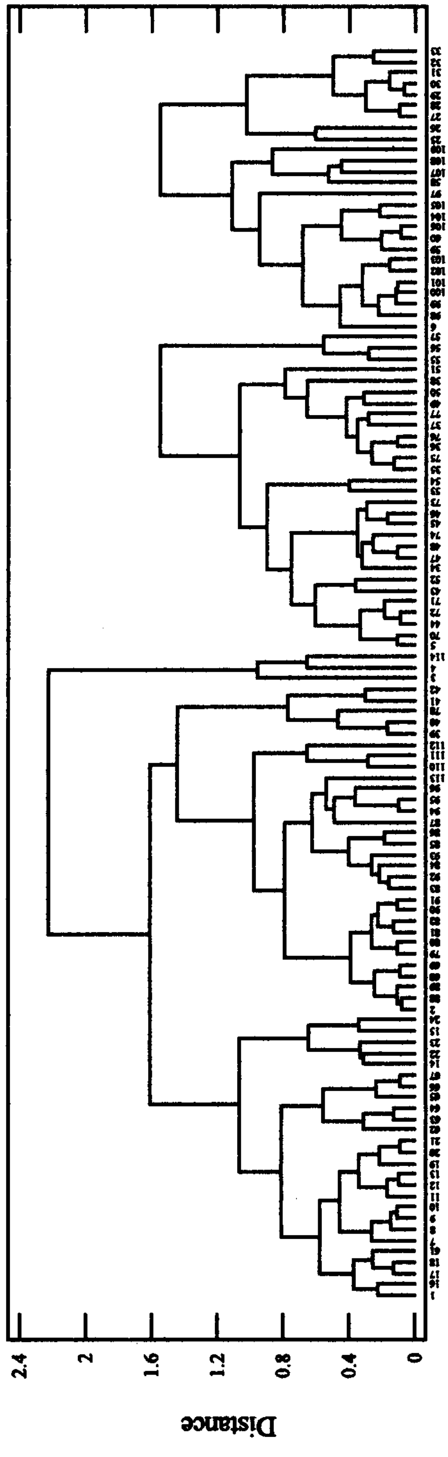

FIGURE 2 Dendogram obtained according to Group Average Method, Euclidean distance.

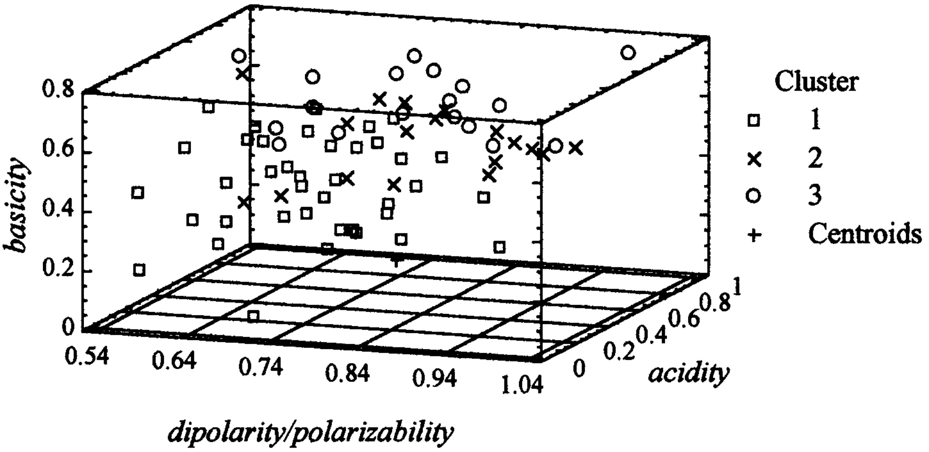

FIGURE 3 Cluster Scatterplot obtained according to Ward's Method, Euclidean distance.

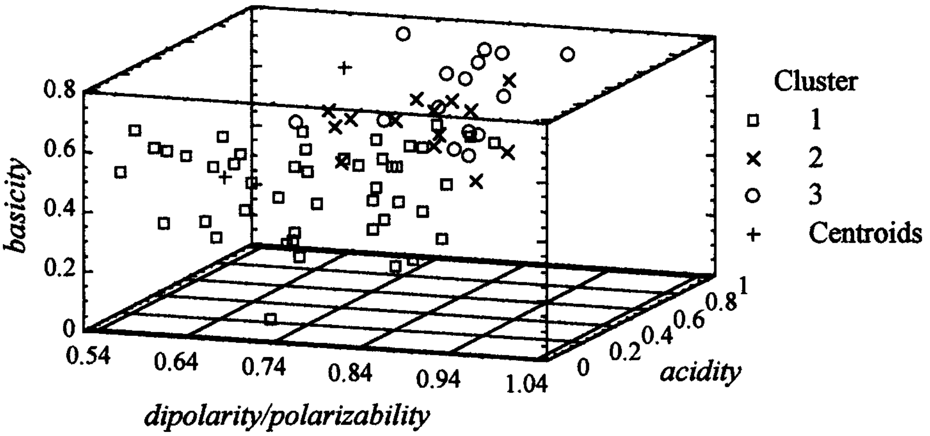

FIGURE 4 Cluster scatterplot obtained according to Group Average Method, Euclidean distance.

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 nonspecific 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 poor 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

TABLE II Cluster information according to the results obtained through the Ward's Method

Method	*Cluster*	*Members*	*Percent*	*Cluster central coordinates*		
				π^*	α	β
WM	1	54	48	0.72	0.21	0.41
	2	31	27	0.89	0.13	0.71
	3	29	25	0.72	0.84	0.62
GA	1	41	36	0.72	0.21	0.43
	2	57	50	0.91	0.16	0.73
	3	16	14	0.70	0.87	0.61

TABLE III Clusters obtained through the application of the Ward's Method

Pure solvents	*Solvent mixtures*			
Cluster 1				
EtAcO	EtAcO + $CHCl_3$	EtAcO + CH_2Cl_2	EtAcO + AcN	$CHCl_3$ + MeOH
AcN	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.5
$CHCl_3$				
CH_2Cl_2	AcN + $CHCl_3$	AcN + CH_2Cl_2		
	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.9		
Cluster 2				
DMSO	DMSO + $CHCl_3$	DMSO + CH_2Cl_2	DMSO + AcN	DMSO + MeOH
	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.1$–0.3
Cluster 3				
MeOH	EtAcO + MeOH	DMSO + MeOH	AcN + MeOH	$CHCl_3$ + MeOH
	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.4$–0.9	$X_{CoS}=0.1$–0.9	$X_{CoS}=0.6$–0.9

TABLE IV Clusters obtained through the application of the Group Average's Method

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

systems show changes in clustering with the mixtures composition, the intersolvents 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.

3. *Application* The often 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 linear solvation energy relationships [11,12]. In earlier articles, 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 [5]. 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 [13–15].

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.

Linear solvation energy relationships We have selected the reported kinetic results corresponding to the reaction of 2,4-dinitrochlorobenzene (2,4-DNClB) with piperidine (PIP) carried out in pure solvents and in some binary mixtures particularly selected (which were grouped in this work by the application of the WM) in order to realize a correlation analysis [5,13,16]. For these reactions, a two-step mechanism has been 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 Kamlet–Taft model: $\log k_A = Y + s\pi^* + a\alpha + b\beta$. The results are presented in Table V. 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.

EXPERIMENTAL

The solvatochromic indicators were prepared and/or purified as previously reported [5]. The solvents were purified as previously reported and were kept over molecular sieves [5]. All binary mixtures were prepared prior to use and stored under anhydrous

TABLE V 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)

$\log k_A = Y + s\pi^* + a\alpha + b\beta$	*Cluster 1*	*Cluster 2*	*Cluster 3*
	EtAcO; $CHCl_3$	DMSO	MeOH
	EtAcO + $CHCl_3$	DMSO + $CHCl_3$	EtAcO + MeOH
	$X_{CoS} = 0.1–0.9$	$X_{CoS} = 0.1–0.9$	$X_{CoS} = 0.1–0.9$
	$CHCl_3$+MeOH	DMSO + MeOH	$CHCl_3$ + MeOH
	$X_{CoS} = 0.1–0.5$	$X_{CoS} = 0.1–0.3$	$X_{CoS} = 0.6–0.9$
$r(r^2)$	0.966 (0.933)	0.937 (0.878)	0.949 (0.901)
SD	0.164	0.115	0.107
$Y(S_Y)$	−1.578 (0.177)	−2.23 (0.317)	1.72 (0.520)
$s(S_s)$	−0.703 (0.275)	0.509 (0.499)	−2.31 (0.323)
$a(S_a)$	−1.90 (0.132)	−0.789 (0.418)	−1.48 (0.294)
$b(S_b)$	3.76 (0.248)	2.76 (0.624)	0.877 (1.03)
n	16	13	14

conditions. For the spectrophotometric measurements, indicator dye solutions of about 5×10^{-5} M (Solutes I and III) and 10^{-4} M (Solute II) were prepared just prior to use. The spectroscopic data were obtained with a Perkin–Elmer model Lambda 40 UV–Vis spectrophotometer, equipped with a thermostatic cell holder.

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