Correlation of acid–base properties of solutes with the polarity parameters and other solvatochromic parameters of dioxane–water mixtures

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Abstract

The behaviour of water–dioxane mixtures as solvents is studied paying special attention to the correlations which may exist among the solvatochromic parameters of these mixtures, as well as to the correlations among some of these parameters and the acid–base properties of model solutes (whose acidity constants are determined). Values of the polarity parameter π^*, proposed by Kamlet and Taft, are determined from measurements of shifts in λ_{max} of 2-nitroanisole, 4-nitroanisole and 4-ethylnitrobenzene, proposed as reference dyes for amphiprotic solvents. The correlations of π^* values with some bulk properties and different microscopic parameters of the working solvents are established. Acid dissociation constants for propionic acid, chosen as a model for aliphatic carboxylic acids, and salicylic acid, for both aromatic carboxylic and phenolic hydroxylic acids, in water–dioxane mixtures are determined from e.m.f. data (at a constant electrolyte concentration 0.2 M and at 25 °C). The solvent composition range studied comprises from 10 to 70% dioxane (vol./vol.). Correlations obtained among the values of acid dissociation constants and the solvatochromic parameters for the solvent mixtures can be useful in helping to explain the variation of the acid–base character of solutes when properties of solvent are modified.

Introduction

Solvent mixtures have become an important subject of research because of their frequent use and the wide field of applications they offer. The most important feature of these mixed solvents is the gradual variation of properties they show when their composition is gradually modified.

A very interesting binary mixture is the water–dioxane mixture, first introduced in solution chemistry by Calvin and Wilson [1] and later used and studied by many authors [2, 3]. The difference between both constituents, especially with reference to their relative permittivity ($\epsilon \approx 78.54$ for pure water and 2.2 for pure dioxane), gives to their mixtures an unusually big span of properties. Thus, many different applications of this solvent mixture exist because of its versatility, among them, the study of the influence of decreasing polarity on certain phenomena related with biologic macromolecules [4] (stacking, hydrophobic interactions,...) or its use as a solvent medium to reach the differentiating titration of various functional groups in certain natural polyelectrolytes (humic and fulvic acids). Many studies have been made to determine macroscopic param-

eters (relative permittivity [5, 6], refraction index,...) or to try to determine the bulk structure of these hydroorganic mixtures, but a lack of investigation of the microscopic characteristics of the cybotactic zone of solutes in these solvents is noticed.

It is well-known fact that certain microscopic phenomena of solutes, such as proton-transfer equilibria, are strongly influenced by the solvent which forms their solvation sphere, which normally does not have the same properties of the bulk solvent nor frequently the same composition. In order to characterize this important zone of the solvent, a new group of microscopic parameters was proposed, the so-called solvatochromic parameters. Microscopic parameters can be determined from the values of many different kinds of properties (kinetic, thermodynamic,....), but the easiest and most commonly used procedure involves the use of some reference dyes, called solvatochromic indicators, whose chromophores change the frequency of their absorption band when the properties of the solvent are modified. Among all the microscopic parameters, the most accepted and used are the following: $E_T(30)$, proposed by Dimroth and Reichardt [7], taken as a solvent polarity measure, and α, β and π^*, proposed by Kamlet and

Taft [8–10], to measure respectively the hydrogen-bond acidity, the hydrogen-bond basicity and the polarity of solvent.

In order to overcome the scarceness of information about the microscopic environment of the solutes in water–dioxane mixtures, the values of the solvatochromic parameters of these solvent systems are determined in the present work and correlations between all of them are proposed or confirmed, according to previous models [11].

Thus, in this work two different kinds of experiments have been carried out: the spectroscopic determination of the π^* parameter for water–dioxane mixtures, (α, β and $E_T(30)$ are already known from previous studies [12–14]) and the e.m.f. determination of the acidity constants of certain model solutes, taken as representatives of different functional groups. Between both sets of results interesting correlations have been obtained that can help to clarify the acid–base behaviour of the solutes in this hydroorganic mixture; behaviour that is clearly influenced by the properties of the cybotactic zone of the solutes.

Experimental

Reagents

Dioxane (PROBUS, a.r.) was purified by Eigenberger's method [15]. Water was deionized and distilled twice over potassium permanganate. 4-Nitroanisole (Merck, z.s.) was purified by active-carbon treatment in an acetone solution and recrystallized from water. 2-Nitroanisole, 4-ethylnitrobenzene and N-methyl-2-nitroaniline from Aldrich (a.r.). Potassium hydroxide (Merck, a.r.) CO_2-free solution in dioxane–water was prepared by the ion-exchange procedure [16]. Salicylic acid (Merck, a.r.) was purified by sublimation. Propionic acid and all other reagents were Merck, a.r.

Apparatus

A Beckman DU-7 spectrophotometer was interfaced (RS232) to an IBM personal computer. Spectra acquisition was controlled through Beckman data capture software. An ORION SA 720 potentiometer (precision ± 0.1 mV) was used. An ORION 90-05 AgCl/Ag reference electrode with a ceramic junction and internal reference solution of sat. KCl in the working hydroorganic mixture was used in conjunction with an ORION 91-01 glass electrode. A double-walled cell was thermostatted at (25 ± 0.1) °C. A Metrohm 665 Dosimat autoburette (precision 0.01 ml) with an exchange unit of 5 cm^3 was fitted with an antidiffusion burette tip. A magnetic stirrer was

used. All of the titration apparatus was connected to a PC computer (HP Vectra ES/12 or HP 9133) through an interface HP 3421A, which allowed the full automatization of the titration process.

Procedure

Determination of the polarity–polarizability π^* parameter

For the determination of the polarity–polarizability π^* parameter of the studied water–dioxane mixtures, 2-nitroanisole (2-na), 4-nitroanisole (4-na), 4-ethylnitrobenzene (4-enb) and N-methyl-2-nitroaniline (Nm2na) were used as solvatochromic indicators. All of them were proposed by Kamlet et al. [10] for use in amphiprotic solvents or amphiprotic mixtures of solvents.

The spectrum of each test solution (a solution of a solvatochromic indicator in a given dioxane–water mixture) is recorded against a blank consisting of a dioxane–water mixture of identical composition as the solvent used in the test solution. Three replicates of each spectrum are obtained from identical independently prepared test solutions. From the digitalized average spectra, the wavelength of the longest-wavelength absorption maximum is determined. For every solvent composition this procedure is followed at three different concentration levels of the indicator. The gross average of the wavelengths of maximum absorption at each solvent composition is taken as the final value for the calculation of solvatochromic parameters.

From the gross average wavelength for each binary mixture, the values for the π^* parameter are obtained by the following expression

$$\pi^* = (\nu - \nu_0)/s$$

where ν is the frequency associated with the experimental wavelength, ν_0 is the frequency of the absorption maximum of the solvatochromic indicator dissolved in cyclohexane ($\pi^* = 0$) and s is the susceptibility of the measured property to changes in the solvent polarity.

Determination of acid dissociation constants in dioxane–water mixtures

Acid protonation constants for propionic acid and salicylic acid were determined from e.m.f. readings. The potentiometric cell used was: GE/working soln., 0.2 M, n% dioxane/RE (KCl$_{sat}$, n% dioxane) where GE is the glass electrode, RE the reference electrode and n is the dioxane percentage in volume in the working mixture. The solvent of the inner solution of the reference electrode has the same composition as that of the working mixture to minimize liquid

junction potential problems which would originate from differences in solvents.

The Gran method [17] was used for *in situ* calibration of the cell and determination of the standard potential of the working electrode. The ionic product of the medium and the pH dependence of the liquid junction potential were also obtained from the strong acid–strong base titrations performed for calibration. For each mixture, the ionic product and the liquid junction potential were determined simultaneously through an iterative process using the MINIGLASS program [18]. Though liquid junction potentials (assumed to be given by expressions such as $E_J = j_H[H^+]$ or $E_J = j_{OH}[OH^-]$ in acid or basic media, respectively [19]) cannot be strictly considered constant with time for a ceramic junction, the small modifications in the value of the coefficient j_{OH} do not affect significantly the pK_a values calculated considering it as a constant, since the use of a ceramic junction minimizes its value and the period of time needed to perform the titrations is rather short. After calibration, a known amount of acid solute whose pK_a is to be determined was added to the cell and the titration continued until the suitable pH value was reached.

For all the deprotonation processes studied, several replicate experiments were performed. The experimental conditions of the titrations performed are listed in Table 1. As the deprotonation of both functional groups of salicylic acid occur in very different pH ranges, they can be studied in separated experiments, starting from salicylic acid or sodium salicylate solutions, depending on the studied process.

In all the titrations, the titrand and the titrant were prepared in solvent mixtures of the same composition and at the same total electrolyte concentration (0.2 M in KNO_3). The working solutions were titrated at 25 °C under a continuous flow of nitrogen.

In order to determine the pK_a values, the numerical analysis of e.m.f. data was carried out using the SUPERQUAD program [20]. The accuracy of the results is indicated by the parameter σ, which represents the ratio of the root mean square of the weighted residuals to the estimated error in the working conditions (0.01 ml for the autoburette volume readings and 0.1 mV for the e.m.f. readings),

TABLE 1. Experimental conditions of potentiometric titrations

Dioxane (%)	System	No. of titrations	Ligand concentration or concentration range (mmol l^{-1})	Range of $-\log[H^+]$
10	Prop-H[a]	4	6.9	3.0–6.5
	Sal$_1$-H[b]	3	5.6	2.5–5.5
	Sal$_2$-H[c]	4	24.8–25.0	10.2–12.5
20	Prop-H	3	6.9	3.5–7.0
	Sal$_1$-H	4	8.0	2.5–6.0
	Sal$_2$-H	4	12.5	10.0–12.6
30	Prop-H	3	34.5	3.5–7.0
	Sal$_1$-H	4	27.8–28.1	2.5–6.0
	Sal$_2$-H	3	12.3	11.0–13.0
40	Prop-H	3	32.8	3.5–7.5
	Sal$_1$-H	3	26.0–26.2	2.5–6.0
	Sal$_2$-H	3	17.9–18.4	11.5–13.3
50	Prop-H	3	32.4–32.6	4.0–8.0
	Sal$_1$-H	3	8.0	3.0–6.0
	Sal$_2$-H	3	17.9–18.0	11.7–13.7
60	Prop-H	3	32.2–32.8	4.0–8.0
	Sal$_1$-H	3	26.1	3.0–6.0
	Sal$_2$-H	3	18.0	12.0–14.0
65	Prop-H	3	34.5	4.5–8.0
	Sal$_1$-H	4	5.6–27.9	3.0–6.3
	Sal$_2$-H	3	17.6–17.8	12.2–14.5
70	Prop-H	3	34.5	5.0–9.0
	Sal$_1$-H	4	27.8	3.0–7.0
	Sal$_2$-H	3	18.0–18.1	12.5–14.7

[a]Propionic-H.   [b]Salicylic-H (−COOH group).   [c]Salicylic-H (−OH group).

and by the value of the statistic parameter χ^2, which is based on weighted residuals of e.m.f. readings [20].

Liquid junction potential, given by $E_J = j_{OH}[OH^-]$, must be taken into account in the calculation only for the deprotonation of the phenolic group of salicylic acid, which occurs in a very basic pH range. In the pH ranges where the deprotonation of carboxylic groups of both propionic and salicylic acids occurs, the influence of the liquid junction potential can be considered negligible.

Results

Table 2 shows the π^* values obtained from each solvatochromic indicator for each composition mixture (average of values obtained at three different concentration levels), and the gross-averaged π^* values, calculated as a mean from the three valid reference dyes, after rejecting the significantly different results of N-methyl-2-nitroaniline.

Table 3 gives the pK_w and j_{OH} values for the different water–dioxane mixtures, at 25 °C and a constant electrolyte concentration 0.2 M, evaluated using the MINIGLASS program.

Table 4 includes the pK_a values for salicylic and propionic acids for the different water–dioxane mixtures, at 25 °C and a constant electrolyte concentration 0.2 M, evaluated using the SUPERQUAD program.

Discussion

It can be observed in Table 2 that N-methyl-2-nitroaniline yields results which are very different from those obtained with the three other indicators. The differences are significant, as proved by the Cheong and Carr graphic method [11, 21]. From the results obtained in the factor analysis of all the data [22], it must be accepted that these differences arise from the effect of hydrogen-bond interactions with the solvent on the spectral shift of this indicator. Therefore, the π^* values obtained with this dye were rejected.

Although the results obtained from each one of the three valid reference dyes show small differences from each other, attributable mainly to differences in their basic character, which is of course very weak in all cases, other parameters proposed as a polarity measure are affected to a much more significative degree by the hydrogen-bond interactions. This is the case of $E_T(30)$, proposed by Dimroth and Reichardt, evaluated from 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide taken as a solvatochromic indicator. The structure of this substance favours the hydrogen-bond interactions between its phenoxide group and hydrogen atoms of the solvent. Thus, $E_T(30)$ is considered to be a mixed measure depending on the polarity of the solvent and also on its hydrogen-bond donor ability. This was observed by Kamlet and co-workers, who proved that $E_T(30)$ is a linear combination of π^* and α [23], which are the parameters proposed by them as a measure of

TABLE 2. π^* values obtained from each solvatochromic indicator tested and averaged π^* values for the different compositions of water–dioxane mixtures

Composition of the solvent mixture		π^*				$\pi^*_{average}$
% dioxane	n_2	4-na	2-na	4-enb	Nm2na[a]	
100	1.000	0.537	0.541	0.543	0.585	0.540
95	0.801	0.637	0.642	0.631	0.706	0.636
90	0.655	0.718	0.714	0.680	0.771	0.704
85	0.545	0.762	0.765	0.718	0.820	0.748
80	0.458	0.787	0.802	0.755	0.870	0.781
75	0.388	0.840	0.836	0.795	0.910	0.823
70	0.330	0.857	0.874	0.815	0.953	0.849
65	0.282	0.890	0.902	0.863	1.017	0.885
60	0.241	0.924	0.935	0.902	1.025	0.920
50	0.174	0.974	1.015	0.978	1.134	0.989
40	0.123	1.042	1.065	1.039	1.227	1.049
30	0.083	1.071	1.113	1.080	1.293	1.088
20	0.050	1.089	1.152	1.132	1.353	1.124
10	0.023	1.106	1.169	1.154	1.366	1.143
5	0.011	1.111	1.177	1.159	1.375	1.149

[a]These values are not included in the final averaged values.

TABLE 3. Ionic product, pK_w, and liquid junction potential coefficient, j_{OH}, for dioxane–water mixtures of 25 °C and a constant electrolyte concentration of 0.2 M, calculated using MINIGLASS program

Dioxane (%)	pK_w	Standard deviation	j_{OH}[a]	Standard deviation
10	13.963	0.004	63	5
20	14.149	0.005	82	22
30	14.3880	0.0004	46	4
40	14.740	0.002	98	3
50	15.100	0.003	103	3
60	15.525	0.005	31	3
65	15.864	0.005	88	2
70	16.09	0.02	80	7

[a]Values of j_{OH} are given in mV l mol^{-1}.

the polarity and the hydrogen-bond acidity of solvent, respectively. The different nature of $E_T(30)$ and π^*, both proposed as polarity measures, can be seen easily from the plot of π^* versus $E_T(30)$ (Fig. 1), where the non-linearity between the homologous values of each parameter is evident.

In a recent investigation, Cheong and Carr [11] confirmed the mixed nature of $E_T(30)$ and proposed the following general equation, valid for several hydroorganic mixtures: $E_T(30) = 31.92(\pm 3.8) + 11.42(\pm 5.6)\pi^* + 15.96(\pm 3.0)\alpha$ (in parentheses, the standard deviation associated to the coefficient).

The relationship obtained for water–dioxane mixtures from a multiple regression analysis using the π^* data obtained in this work agrees with the Cheong and Carr equation and can be expressed as follows:

$$E_T(30) = 31.75 + 10.83\pi^* + 18.06\alpha$$

standard deviation $= 0.295$ $\quad r = 0.9992$

As a consequence of the mixed nature of $E_T(30)$, which is sensitive to many solute–solvent interactions, this parameter has been used to investigate the phenomena of preferential solvation in many binary mixtures [24, 25].

According to Dawber et al. [25], if the components of a binary solvent mixture participate randomly in the solvation of the solute, a linear relationship analogous to the Raoult law is expected: $E_T(30)_{mixture} = \Sigma X_i E_T(30)_i^0$, where $E_T(30)_i^0$ is the value

TABLE 4. Values of logarithm of protonation constants for propionic and salicylic acids at 25 °C and a constant electrolyte concentration of 0.2 M, in water–dioxane mixtures, calculated using SUPERQUAD program

Dioxane (%)	System	$\log K$	Standard deviation	σ	χ^2
10	Prop-H[a]	4.825	0.003	1.534	17.64
	Sal$_1$-H[b]	2.897	0.001	1.590	23.26
	Sal$_2$-H[c]	12.789	0.008	1.952	18.35
20	Prop-H	5.091	0.006	2.235	24.36
	Sal$_1$-H	3.067	0.003	1.482	7.07
	Sal$_2$-H	13.23	0.02	1.010	4.19
30	Prop-H	5.395	0.001	2.450	37.26
	Sal$_1$-H	3.318	0.002	2.863	49.95
	Sal$_2$-H	13.43	0.02	1.006	16.23
40	Prop-H	5.6762	0.0006	1.722	28.48
	Sal$_1$-H	3.524	0.003	2.354	17.33
	Sal$_2$-H	13.51	0.02	2.052	1.55
50	Prop-H	6.063	0.001	3.423	18.63
	Sal$_1$-H	3.789	0.006	2.736	5.67
	Sal$_2$-H	13.94	0.02	1.604	4.95
60	Prop-H	6.4940	0.0005	1.275	32.69
	Sal$_1$-H	4.305	0.001	2.318	18.69
	Sal$_2$-H	14.12	0.02	2.086	4.67
65	Prop-H	6.745	0.001	2.195	6.01
	Sal$_1$-H	4.478	0.003	2.359	56.41
	Sal$_2$-H	14.46	0.01	1.365	4.84
70	Prop-H	6.879	0.002	2.980	41.77
	Sal$_1$-H	4.654	0.001	2.830	17.48
	Sal$_2$-H	14.84	0.02	3.228	27.41

[a]Propionic-H.   [b]Salicylic-H (−COOH group).   [c]Salicylic-H (−OH group).
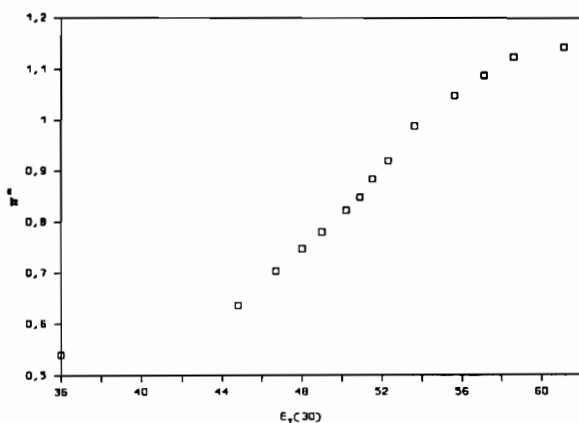
Fig. 1. Plot of π^* vs. $E_T(30)$ for water–dioxane mixtures. π^* values were taken from Table 1; $E_T(30)$ values are from the literature [12, 13].
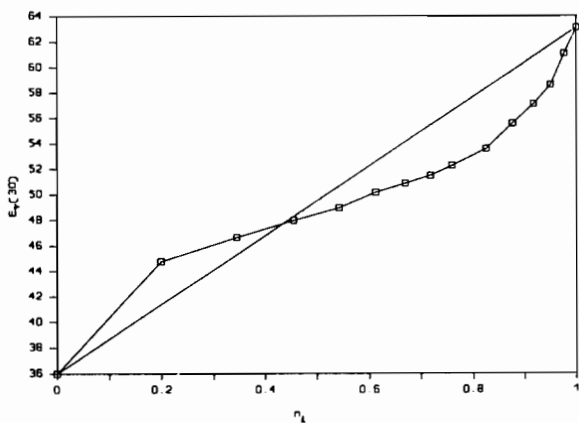

Fig. 2. Plot of $E_T(30)$ vs. n_1 for water–dioxane mixtures for an ideal behaviour ($-$) and for experimental values ($\square$).

of the parameter for each pure solvent and X_i is the respective molar fraction in the solvent mixture. From the plots of $E_T(30)_{mixture}$ versus n_1 (1 being the more polar constituent of the solvent mixture), the existence of preferential solvation can be seen when a loss of linearity is produced ('preferential' meaning the presence in the cybotactic zone of a higher content of the constituent than that predicted by the linearity assumption).

In the case of water–dioxane mixtures (Fig. 2), a double behaviour is noticed. If this assumption is correct, for solutions with $n_2 < 0.55$ (% dioxane < 85), the preferential solvation is due to dioxane, and for higher percentages of this cosolvent, water is the constituent responsible of this phenomenon.

Knowledge of the different microscopic parameters of dioxane–water mixtures and the existence of cor-

relations as above allow an approach to be made to the properties and structure of the cybotactic zone of solutes. It would be interesting to compare these characteristics with those present in the bulk of these solvent mixtures.

In the plot of $1/\epsilon$ versus π^* (Fig. 3), both taken as pure measures of polarity, the first one referring to the bulk of the solvent and the second one related with the cybotactic zone of the solute, a colinearity can be observed for $\epsilon > 23$ ($1/\epsilon < 0.037$), i.e. for percentages of dioxane (vol./vol.) < 60%, approximately. When values of ϵ decrease, that is, for higher percentages of dioxane, a clear deviation of the linearity can be detected. This means that in mixtures richer in dioxane (% dioxane > 60), the polarity varies in a different way than in mixtures poorer in this cosolvent. The behaviour shown by the Figure points to an increased polarity of the cybotactic zone (measured by π^*) in mixtures richer in dioxane in comparison with the predicted value given by the linear correlation found for the poorer mixtures. These different properties of the bulk solvent and the solvation sphere may be the reason for the inadequacy of certain theories that try to explain the proton-transfer microscopic process as a function only of macroscopic properties of the solvent mixture, as n_2 or $1/\epsilon$.

Thus, in the plot of pK_w values (Table 3) or pK_a values of propionic and salicylic acid (Table 4) versus molar fraction of dioxane (Fig. 4) or $1/\epsilon$ (Fig. 5) it can be seen that no linear correlations are obtained that are valid for the whole range of studied compositions. It is in the zone in which deviations start to be observed where the specific solute–solvent interactions become more important and the ineffectiveness of an only macroscopic model more evident.
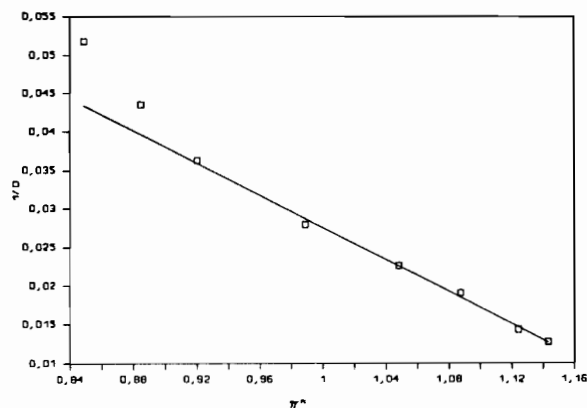

Fig. 3. Plot of $1/\epsilon$ vs. π^* for water–dioxane mixtures. π^* values are those from Table 1; ϵ values are taken from the literature [6].

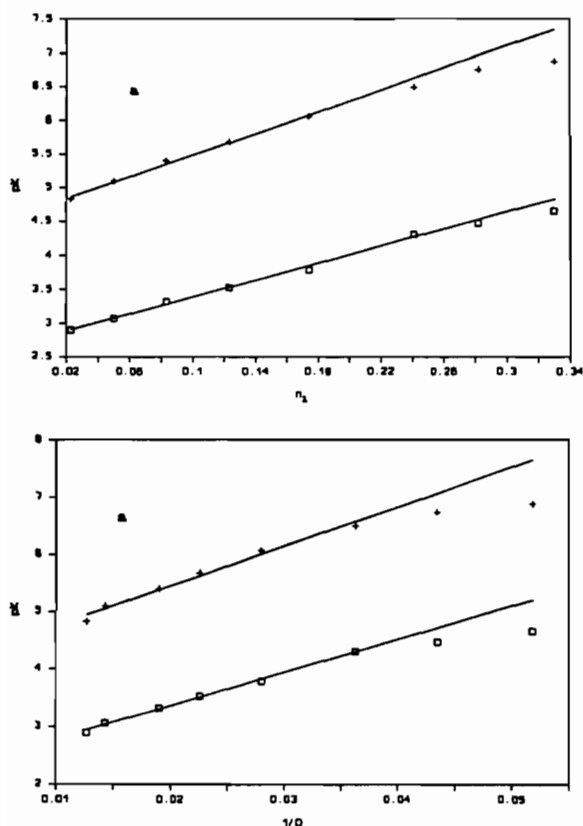Fig. 4. Plot of pK_a values of (a) carboxylic groups of salicylic acid (□) and propionic acid (+); (b) phenolic group of salicylic acid (□) and pK_w values (+) vs. molar fraction of dioxane.

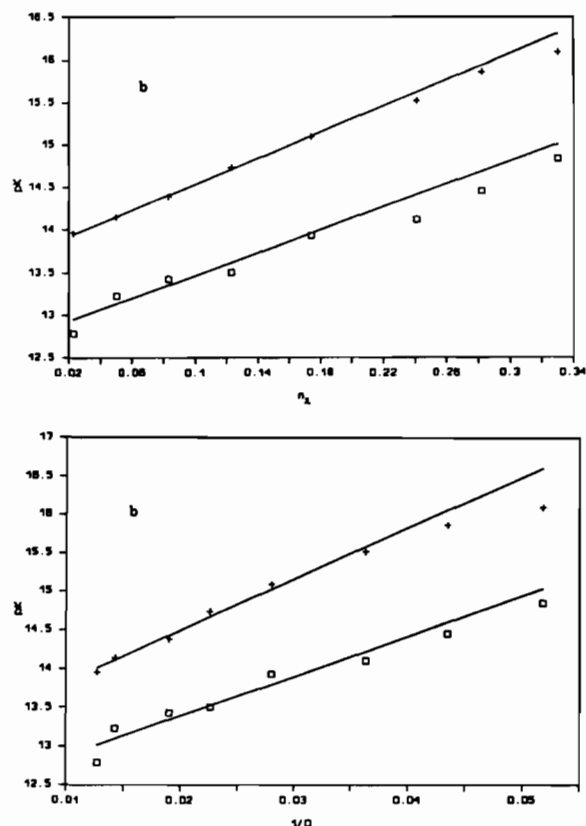Fig. 5. Plot of pK_a values of (a) carboxylic groups of salicylic acid (□) and propionic acid (+); (b) phenolic group of salicylic acid (□) and pK_w values (+) vs. $1/\epsilon$ for water–dioxane mixtures.

So, research which could lead to expressions that relate the acidity constants of solutes with the properties of their immediate environment, well-characterized by the microscopic parameters, is justified.

When the plots of pK_w and pK_a values versus $E_T(30)$ (Fig. 6) are depicted two linear segments can be observed, whose intersection is between 50 and 60% of dioxane. The different behaviour of both zones can be attributed to the breakdown (detected by Langhals [12]) of the hydrogen-bridged structure of water by dioxane when the amount of this cosolvent begins to be high. Since it has been previously proved that $E_T(30)$ measures the polarity and the hydrogen-bond donor acidity of the solvent and since this last property will change strongly with the destruction of the water structure, it is clear that two differentiated trends will result in the behaviour of acid solutes, well noticeable in the last mentioned Figures.

A more general approach is that of Kamlet and Taft, who suggested a general equation [10] which explains any solute property varying with solvent composition as a linear combination of the microscopic parameters of the solvent responsible for the modification of the solute property studied. This general equation has also been applied to solvent mixtures and is expressed very commonly as follows [10]: $XYZ = (XYZ)_0 + a\alpha + b\beta + s\pi^*$, where α, β and π^* are the microscopic parameters previously described, XYZ is the solute property, XYZ_0 the value of this property for the same solute in a hypothetical solvent for which $\alpha = \beta = \pi^* = 0$, and a, b and c are numerical coefficients related with the susceptibility of the studied solute property to changes in α, β and π^*, respectively. This equation can include additional terms or some of its terms can become equal to zero depending on the property of the solute to be described [26].

In the present work, several attempts have been made to find the best form of the Kamlet and Taft equation to describe the variation of pK values (for both the autoprotolysis and the acid dissociation processes) in water–dioxane mixtures.

Multiple regression analysis has been applied to our data. All possible combinations of solvatochromic parameters have been checked. The best fit is obtained when only the π^* parameter is used, yielding
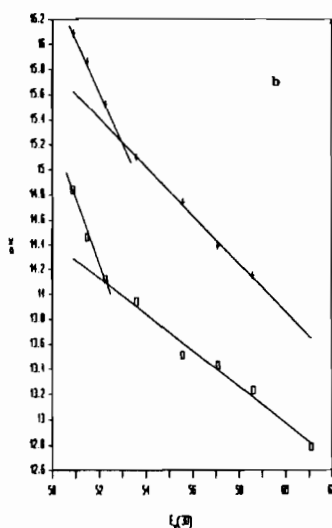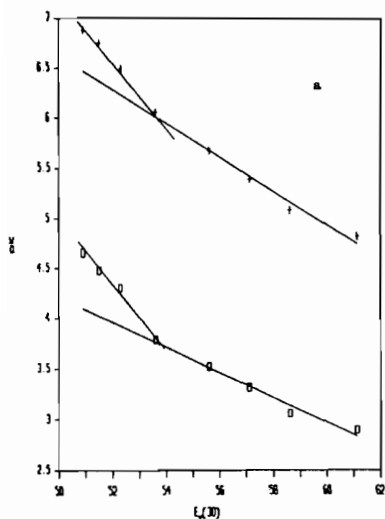
Fig. 6. Plot of pK_a values of (a) carboxylic groups of salicylic acid (□) and propionic acid (+); (b) phenolic group of salicylic acid (□) and pK_w values (+) vs. $E_T(30)$ for water–dioxane mixtures.

the following general equation

$$pK = s\pi^* + pK^0$$

For each one of the systems studied, this equation becomes

$$pK_{1sal} = -5.9(\pm 0.1)\pi^* + 9.68(\pm 0.04) \qquad r = 0.998$$
$$pK_{2sal} = -5.9(\pm 0.5)\pi^* + 19.7(\pm 0.1) \qquad r = 0.981$$
$$pK_{prop} = -6.8(\pm 0.3)\pi^* + 12.77(\pm 0.08) \qquad r = 0.995$$
$$pK_w = -7.1(\pm 0.1)\pi^* + 22.10(\pm 0.04) \qquad r = 0.998$$

(in parentheses, as before, the standard deviation associated with the coefficient).

These simple equations explain well all the experimental data within the composition range studied. If the three solvatochromic parameters are forced
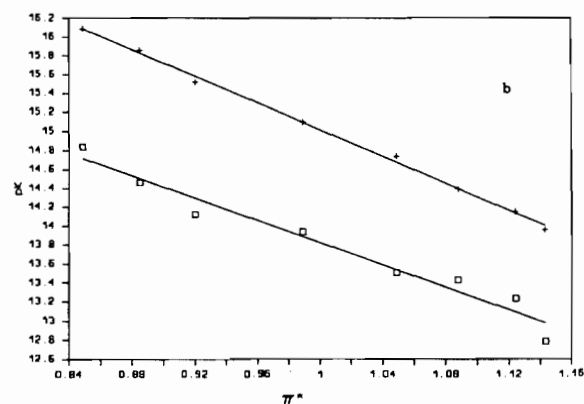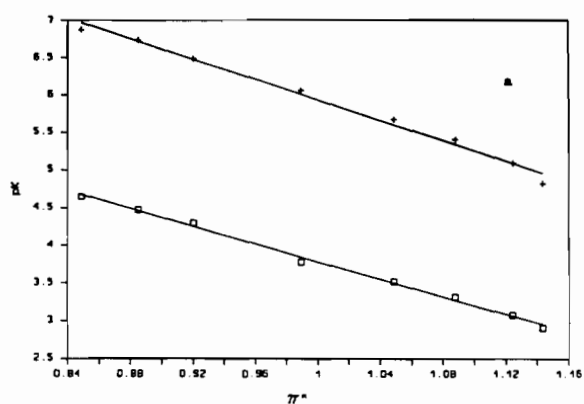

Fig. 7. Plot of pK_a values of (a) carboxylic groups of salicylic acid (□) and propionic acid (+); (b) phenolic group of salicylic acid (□) and pK_w values (+) vs. π^* for water–dioxane mixtures.

into the equation, no improvement is obtained in the fit. For instance, for the first acid dissociation of salicylic acid, the equation would be:

$$pK_{1sal} = -0.4(\pm 1)\alpha - 1(\pm 5)\beta - 6(\pm 2)\pi^* + 11.4$$

$$r = 0.997 \quad r_\alpha = 0.167$$
$$r_\beta = 0.155$$
$$r_\pi = 0.895$$

The small coefficients in the α and β terms and the big error associated with them, as well as the small partial correlation coefficients for these two parameters, confirm that their contribution in the description of the variation of pK values in water–dioxane mixtures can be neglected.

Thus, a really useful correlation is finally found, that shows the linear dependence of acid dissociation constants with the microscopic polarity of solvent (expressed by π^*) for the whole range of compositions in water–dioxane mixtures (Fig. 7). The previous correlation, which considered $1/\epsilon$ as a measure of polarity, has been modified by the introduction of the microscopic character of this solvent property,

defined by π^* parameter, which so strongly affects the proton-transfer process.

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