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Investigation of a linear solvation free energy relationship between pKas of PAR and solvatochromic parameters of binary mixture of water-nonaqueous solvents

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ABSTRACT

A linear solvation free energy relationship has been conducted to study the effects of solvent and solute properties on the acidity constants of 4-(2-pyridylazo) resorcinol (PAR) in different solvent mixtures. Dissociation constant values of PAR were collected from the literature in 90-0.0 (wt. %) of methanol, 70-0.0 (wt. %) of dioxane, 80-0.0(wt. %) of acetonitrile (AN) and 80-0.0 (wt. %) of dimethylformamide (DMF) mixed with water at 298.5 K. The data set were gathered in a matrix submitted to multiple linear regression analysis in order to obtain the number of factors which affects the variation of the whole data sets. The SPSS software was used for the selection of the variables that resulted in the best-fitted models. To model the solvatochromic parameters multiple linear regression (MLR) was applied to identify the important factors. The pKa values were correlated with just one of the Kamlet and Taft solvatochromic parameters (π*) of mixtures of methanol, dioxane, acetonitrile and DMF with water. The proposed equation allows prediction of pKa values of PAR in any mixture of methanol-water, dioxane-water, acetonitrile-water and DMF-water.

KEYWORDS

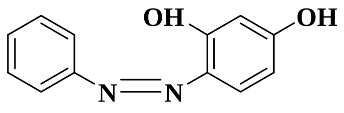
LSFER;
Dissociation constants;
MLR;
Solvatochromic parameters;
Nonaqueous solvents.

1. INTRODUCTION

The solvatochromic parameters are intended for use in linear solvation energy relationships (or, in the case of solute/solute interactions, linear complexation energy relationships) of the generalized form

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H^2 \qquad (1)$$

This equation may be reduced to a more manageable form by a judicious choice of solvents and reactants or indicators. One-, two- and three-parameter correlations involving different combinations of the above parameters and various types of physicochemical properties are demonstrated. Where XYZ is the solvent dependent property studied of the solute, $(XYZ)_0$ is the value of this property for the same solute in a hypothetical solvent for which $\alpha = \beta = \pi^* = \delta_H^2 = 0$. The π* scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect[1-4]. The α scale of solvent HBD (hydrogen-bond donor) acidity describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bonds[1,5-7]. The β scale of solvent HBA (hydrogen-bond-acceptor) basicity provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond[1,8-11]. The β scale has also been used to evaluate hydrogen-bond-acceptor strengths of solid HBA bases dissolved in non-HBA solvents[1,12]. The δ parameter in (Eq.1) is a 'polarizability correction term' equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. The δ_H^2 term in (Eq.1) is the Hildebrand solubility parameter[13], a measure of the sol



SCHEME 1

vent/solvent interactions that are interrupted in creating a cavity for the solute (the cavity term), and is important when dealing with enthalpies or free energies of solution. The s, d, a, b and h coefficients in (Eq.1) measure the relative susceptibilities of XYZ to the indicated solvent property scales. When the property correlated does not involve significant changes in the cavity volumes, as is the case of its different binary mixtures with the same solvents, the term δ_H^2 drops out of (Eq.1). An appropriate form of (Eq.1) to dissociation constant value would be:

$$\mathbf{pKa = pKa_0 + s\pi^* + a\alpha + b\beta} \qquad (2)$$

This equation can include additional terms and some of its terms can equal to zero, depending on the series of solutes to be described[14]. Several attempts can were made to find the best form of the Kamlet–Taft equation to describe the variation of pKa values[15]. However, methanol, dioxane, acetonitrile and DMF have weaker solvatochromic characteristics than water[16]. Thus they show weaker solvation power than water[17].

Mixed solvents are interesting, because two solvents mixed together produce a solvent with quite different properties, both, physically (dielectric, density and viscosity) and chemically (acid-base and donor-acceptor properties). As far as the acid–base properties are concerned, an important feature is that the nature of the solvent is crucial for the strength of acids and bases. In particular, important is the proton affinity, in other words, the proton-donating and proton-accepting properties of solvent, as well as its polarity. In addition, the ionization degree of solute depends on the dielectric constant of solvent. Media of high dielectric constants are strongly ionizing, whereas those of low dielectric constants ionize to a lesser extent[18]. By mixing solvents of different polarity in proper ratios, dielectric constant of the medium can be varied and, at the same time, the strength of dissolved acids and bases[19]. It should also be emphasized that solvents mixtures can be more convenient than individual solvents owing to enhanced solubility efficiency, increased sharpness of color change of indicators during titration and more manageable shape of acid-base titration curves[20-22].

PAR (SCHEME 1) in the free acid form (H_2L) is an orange-red to brown amorphous powder. It is slightly soluble in water (5mg/100ml) and alcohol, but is more soluble in acidic or alkaline solution[23]. The proton dissociation scheme can be represented as below:

$$\mathbf{H_3L^+ \xleftrightarrow{pK_{a1}} H_2L \xleftrightarrow{pK_{a2}} HL^- \xleftrightarrow{pK_{a3}} L^{-2}} \qquad (3)$$

H_3L^+(pH<2.5) and H_2L (pH 3-5.5) are yellow, HL^-(pH 6-12.5) is orange and L^{2-}(pH >12.5) is red. The dissociation constants are pK_{al} = 3.1(o-OH), $pK\alpha_2$ = 5.6 (p-OH) and $pK\alpha_3$ = 11.9 (=NH^+)[24,25]

In this study, a set of pKas of PAR in different percentages of water and four nonaqueous solvents were used to build a model. The MLR with SPSS variable selection method were used to model pKa with the solvatochromic parameters.

2. Theory

Chemical systems are typically multivariate, i.e. multiple measurements are made simultaneously. Therefore, most chemometrics methods fall under the class of statistical techniques known as multivariate analysis. The measurement and analysis of dependence between variables is fundamental to multivariate analysis[26].

2.1. Multiple linear regression (MLR)

In solvatochromic linear solvation free energy Relationship (LSFER), solvatochromic parameters (x) are correlated with one or more response variable (γ). If it is assumed that the relationship is well represented by a model that is linear in the regressor variables, a suitable model maybe

$$\mathbf{y = b_0 + b_1x_1 + b_2x_2 + ... + b_px_p} \qquad (4)$$

In this equation b_0 is the regression coefficient for the intercept and the b_i values are the regression coefficients computed from the data. The algebraic MLR model is defined in Eq. (4) and in matrix notation:

$$\mathbf{Y = Xb + b0} \qquad (5)$$

It is convenient to write the above equation in matrix formulism:

$$\begin{bmatrix} \mathbf{Y_1} \\ \mathbf{Y_2} \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{Y_n} \end{bmatrix} = \begin{bmatrix} \mathbf{X_{11}} & \mathbf{X_{12}} & \cdots & \mathbf{X_{1n}} \\ \mathbf{X_{21}} & \mathbf{X_{22}} & \cdots & \mathbf{X_{2n}} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \mathbf{X_{n1}} & \mathbf{X_{n2}} & \cdots & \mathbf{X_{nn}} \end{bmatrix} \begin{bmatrix} \mathbf{b_1} \\ \mathbf{b_2} \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{b_n} \end{bmatrix} \qquad (6)$$

A nonzero intercept can be included in the multicomponent case by augmenting the X matrix of equation (6) with a column of 1's and the b matrix with a row of b_0. The matrix equation becomes[27]:

$$\begin{bmatrix} Y_1 \\ Y_2 \\ \cdot \\ \cdot \\ \cdot \\ Y_n \end{bmatrix} = \begin{bmatrix} X_{11} & X_{12} & \cdots X_{1n} & 1 \\ X_{21} & X_{22} & \cdots X_{2n} & 1 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ X_{n1} & X_{n2} & \cdots X_{nn} & 1 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ \cdot \\ \cdot \\ b_n \\ b_0 \end{bmatrix} \qquad (7)$$

When X is full rank the least squares solution is: $\hat{b} = (X^T X)^{-1} X^T Y$ where $\hat{b}$ is the estimator for the regression coefficients in $\hat{b}$. The coefficients were obtained through multiple linear regression (MLR)[28].

3. Computer hardware and software

All calculations were run on a pentium IV personal computer with windows XP operating system. To obtain the important factors which affect the variation of the whole data sets we have used SPSS software (SPSS ver. 11.5, SPSS Inc.) and other calculations were performed in the MATLAB (version 7.0, MathWorks, Inc.) environment.

4. Data set

The dissociation constants of PAR data employed in this study were collected from the literature[22,29,30,31]. These dissociation constants are summarized in TABLE 1. Values of the Kamlet-Taft solvatochromic parameter (α, β, π*) for pure solvent are summarized in TABLE 2[16] and the solvatochromic parameters for mixtures were calculated and listed in TABLE 3. SPSS software, was used for variables selection with MLR regression method. Finally we obtained a one factor which keeps most interpretive information for pKa.

5. RESULTS AND DISCUSSION

The data shown in TABLE 1 clearly illustrate the important influence of the nature of the solvent on the dissociation reactions. It has been shown that the solvating ability[32] (as expressed by the Gutmann donicity scale) and dielectric constant of the solvent play a fundamental role in dissociation reactions. Water is a solvent of high solvating ability (i.e. donor number DN = 33.0) and dielectric constant (ε= 78) which can dissociate the acid and stabilize the produced anion and hydrogen ion. It is interesting to note that there is actually a linear relationship between the pKa of three dissociation steps (first step decreases and second and third steps increase). It has been reasonably assumed that preferential solvation of the charged particles by water is mainly responsible for such a monotonic dependence of the acidity constants of PAR on the solvent composition.

It is clear that the dissociation of an uncharged acid in a solvent requires the separation of two ions of opposite charges. The work required to separate these charges is inversely proportional to the dielectric constant of the solvent. The energy required for dissocia

TABLE 2: Solvatochromic parameters of pure solvents; methanol, dioxane, acetonitrile, DMF and water

Solvent	α	β	π*
Methanol	0.98	0.66	0.60
Doxane	0.00	0.37	0.49
Acetonitrile	0.19	0.40	0.66
DMF	0.00	0.69	0.88
Water	1.17	0.47	1.09

TABLE 1 : Dissociation constants of PAR in four binary mixtures (methanol-water), (dioxane-water), (acetonitrile-water) and (DMF-water)

Mixture	pKa1	pKa2	pKa3
90%(m+w)*	2.4	6.82	12.77
80%	2.5	6.69	12.68
70%	2.57	6.52	12.57
60%	2.65	6.35	12.45
50%	2.72	6.28	12.4
40%	2.8	6.11	12.37
30%	2.88	5.97	12.22
20%	2.9	5.86	12.21
10%	3.01	5.8	12.11
0.00%	3.07	5.5	12.04
70%(d+w)*	2.04	7.78	12.88
60%	2.21	7.13	12.18
50%	2.48	6.56	12.3
40%	2.5	6.08	12.19
30%	2.78	5.84	12.32
20%	2.82	5.61	12.24
10%	2.97	5.71	12.27
80%(a+w)*	2.33	7.52	14.6
70%	2.28	7.12	14.7
60%	2.43	6.94	14.5
50%	2.41	6.67	13.2
40%	2.42	6.48	13
30%	2.47	6.27	13
20%	2.78	5.94	13.1
10%	2.75	5.61	12.2
80%(f+w)*	2.29	7.11	12.9
70%	2.4	6.94	13.05
60%	2.61	6.81	13.01
50%	2.66	6.35	12.6
40%	2.7	6.38	12.62
30%	2.71	5.72	12.32
20%	2.79	5.78	12.39
10%	2.82	5.91	12.14

***m = methanol; d = dioxane; a = acetonitrile; f = DMF, w = water**

TABLE 3 : Solvatochromic parameters of four binary mixtures (methanol-water), (dioxane-water), (acetonitrile-water) and (DMF-water)

Mixture	α	β	π*
90%(m+w)*	0.999	0.641	0.649
80%	1.018	0.622	0.698
70%	1.037	0.603	0.747
60%	1.056	0.584	0.796
50%	1.075	0.565	0.845
40%	1.094	0.546	0.894
30%	1.113	0.527	0.943
20%	1.132	0.508	0.992
10%	1.151	0.489	1.041
0.0%	1.17	0.47	1.09
70%(d+w)*	0.351	0.4	0.67
60%	0.468	0.41	0.73
50%	0.585	0.42	0.79
40%	0.702	0.43	0.85
30%	0.819	0.44	0.91
20%	0.936	0.45	0.97
10%	1.053	0.46	1.03
80%(a+w)*	0.386	0.414	0.746
70%	0.484	0.421	0.789
60%	0.582	0.428	0.832
50%	0.68	0.435	0.875
40%	0.778	0.442	0.918
30%	0.876	0.449	0.961
20%	0.974	0.456	1.004
10%	1.072	0.463	1.047
80%(f+w)*	0.234	0.646	0.922
70%	0.351	0.624	0.943
60%	0.468	0.602	0.964
50%	0.585	0.58	0.985
40%	0.702	0.558	1.006
30%	0.819	0.536	1.027
20%	0.936	0.514	1.048
10%	1.053	0.492	1.069

***m = methanol; d = dioxane; a = acetonitrile; f = DMF, w = water**

TABLE 4 : Linear salvation energy relationships for different binary mixtures

Mixture	Linear solvation energy relationships	Regression coefficient (R^2)
Methanol-water	$Pk_1 = 1.46 + 1.49\pi^*$	0.994
	$pK_2 = 8.63 - 2.81\pi^*$	0.989
	$pK_3 = 13.79 - 1.62\pi^*$	0.982
Dioxane-water	$pK_1 = 0.48 + 2.41\pi^*$	0.964
	$pK_2 = 10.82 - 5.16\pi^*$	0.903
	$pK_3 = 13.25 - 1.07\pi^*$	0.911
Acetonitrile-water	$pK_1 = 0.75 + 1.96\pi^*$	0.914
	$pK_2 = 11.75 - 5.77\pi^*$	0.988
	$pK_3 = 20.70 - 7.98\pi^*$	0.985
DMF-water	$pK_1 = -1.09 + 3.74\pi^*$	0.940
	$pK_2 = 16.03 - 9.70\pi^*$	0.914
	$pK_3 = 18.67 - 6.07\pi^*$	0.927

tion is supplied by solvation of the ions, and also the proton transfer from acid to the solvent molecule supplies an additional energy. If the dielectric permittivity and the solvating ability of the solvent are decreased, more energy will be required to separate the anion and cation, and consequently the extent of dissociation of the acid will be lowered. Therefore, the decrease in the pKa of the first step and the increase in those of the second and third steps are due to increasing the mole fraction of methanol, dioxane, acetonitrile and DMF in the binary mixed solvent.

Multiple linear regression (MLR) is one of the most used modeling method. The program used for MLR analysis was written in SPSS. In TABLE 4, Kamlet-Taft equations obtained from the results provided by application of MLR analysis on the data matrices are shown. As emphasized by Abraham[33], goodness of fit is necessary, but not sufficient, the coefficients, which mirror specific properties of the solubilization environment of the solute, must also conform to correct chemical principles. Thus, in the present case, the magnitude and signs of the coefficients should be compatible with the process of transferring hydrogen ion from acid molecule to the bulk solvent. This study confirms the usefulness of microscopic parameters, such as π*, in explanation of microscopic processes, as the solvent properties in the cybotactic zone are the ones which affect directly the solutes when a process such as acid-base equilibrium occurs. The correct reproduction of the studied data matrices using π* and unity (see TABLE 4) implies that the general equation is reduced to only two terms. The solvent polarity is identified as the main cause of pKa values variation of data matrices in methanol-water, dioxane-water, acetonitrile-water and DMF-water mixtures. The coefficients of factor π* in the reduced Kamlet-Taft equations summarized in TABLE 4 are positive for pKa_1 of PAR in all mixtures, which means that an increase in the polarity of the mixed solvent increases the pKa values. Thus an increase in the polarity increases the solvation of the cationic acid ($H_3A^+ \rightarrow H^+ + H_2A$) and decreases dissociation. The dissociation process in methanol-water, dioxane-water, acetonitrile-water and DMF-water is governed by electrostatic interactions (solvation effects). The coefficients of factor * in the reduced Kamlet-Taft equations summarized in TABLE 4 are negative for pKa_2 and pKa_3 of PAR in all mixtures, which means that an increase in the polarity of the mixed solvent decreases the pK values. Thus an increase in the polarity increases the solvation of the ions and therefore dissociation. In the dissociation of neutral and anionic acids, charges are created ($H_2A \rightarrow H^+ + HA^-$) and ($HA^- \rightarrow H^+ + A^{2-}$) and the dissociation process is disturbed when the po larity of medium decreases with the increase in co-solvent (methanol, dioxane, acetonitrile or DMF) content. Hence for dissociation of PAR, electrostatic interaction overwhelms other effects and this fact is reflected in the greater magnitude of π^* coefficients in the Kamlet-Taft equations.

6. CONCLUSION

MLR technique was applied to identify and quantify those solvent parameters that control the dissociation constants of PAR in different mixtures. Several attempts were made to find the best form of the Kamlet-Taft equation to describe the variation of the pK values of PAR in four binary mixtures. All possible combinations of solvatochromic parameters were checked. The best fit was obtained when unity and π^* were used, providing the general equations in TABLE 4. The linear solvation energy relationships obtained, permit the pK values of PAR in any percentage in the range studied of methanol-water, dioxane-water, acetonitrile-water and DMF-water to be known. The equations obtained enable the pK values of PAR studied in any binary mixtures that cited above, to be obtained and thus permit the interpretation of their acid-base behaviour in these widely used hydro-organic mixtures.

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