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INVESTIGATIONS OF SOLVENT PARAMETERS ON ACIDITY DISSOCIATION CONSTANTS OF BROMOCRESOL PURPLE IN WATER-DIOXANE MEDIA

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ABSTRACT

The acidity constants (pKa) of bromocresol purple in various water-dioxane mixtures were determined. The proposed approaches allow prediction of pKa values of bromocresol purple in any mixture of water-dioxane. The results were discussed in terms of the solvent characteristic. The pKa values of the investigated indicator were found to be largely dependent on the ratio of dioxane. This result is confirmed by linear correlation between mol fraction of dioxane and acidity constant due to the solvation of bromocresol purple with both water and dioxane molecules in all binary mixtures. The results showed non-linear relationship between pKa values and reciprocal relative permittivity that indicates both the electrostatic and non-electrostatic which affecting on the acidity constant. A linear solvation free energy relationship was used to study the effects of solvent and solute properties on the acidity constants in some dioxane solvent mixtures. The pKa values were correlated with the Kamlet-Taft solvatochromic parameters of mixtures from water with dioxane. It was mainly affected by non-electrostatic solute-solvent interactions. The KAT multi-parameter correlations represent significant improvements with regard to single- or dual-parameter models with highest F-static.

Keywords: *bromocresol purple, Kamlet-Taft parameters, dioxane,* E_T^N*, LSERs.*

INTRODUCTION

The acid-base equilibria of the species that exit in solutions at various pH's are widely studied spectrophotometrically. For various acid-base indicators, which have different functional groups, there is a marked spectral change with the pH variation of the solution [1 - 3]. The electronic spectral data are used to estimate the acidity dissociation constant of the indicators under investigation. The values of the acidity constant are evaluated at 25°C by means of the linear dependencies between the absorbance and the pH [4]. Acidity constants are essential parameters to the imply extent of ionization of molecules in solution at specific pH values. The acidity constants of organic reagents play essential function in a lot analytical procedures such as acid-base titration, solvent extraction, complex formation, and ion transport. The acid-base properties are affected on the toxicity, chromatographic retention behavior and pharmaceutical properties of organic acids or bases. Much of the theoretical foundation of recent chemistry is predicated on the observation of the effects on acid-base equilibrium of changing molecular structure [5, 6].

As the best means to purposefully affect the protolytic properties of phenols the variations within the solvent composition could also be regarded especially when using binary mixtures of water with aprotic solvents, which could alter the acidity constants of phenolic groups by 5 - 8 orders of magnitude [7]. Among the most important aprotic solvents is dioxane, which has a high dissolving power in relevancy phenolic compounds because of the high basicity. These solvents are widely used in the chemistry of plant materials in pure form and in mixtures with water [8, 9]. Therefore, the mixing solvents of several polarities in suitable ratios, relative permittivity of the medium can be varied and, at the same time, the strength of dissolved acids and bases. The strength of acids is different action that caused by the selective preferential solvation of both phenol molecules and conjugated phenolate anions [8].

Bromocresol purple (BCP, phenol, 4, 4′-(3H-2, 1-benzoxathiol-3-ylidene) *bis* [2-bromo-6- methyl-S, S-dioxide) (Fig. 1) is an acid-base indicator with 90 % content of dye [10]. Bromocresol purple which exists in two main forms in aqueous solutions: single dissociated HIn^- at pH lower than 6.0 with yellow color and double dissociated In^{-2} at pH higher than 6.0 with violet color. The visual color change in the solution at a specific pH is resulting from a distinction with inside the resonance structures, thus, which happens through proton exchange from bromocresol purple to water or vice versa [11, 12]. It is also used to estimate the Human serum-albumin levels in blood by using the spectrophotometric technique [13, 14].

In this work, examination the influence of solvent compositions on the acid-base equilibria of bromocresol purple, which the acidity constants in various aqueous dioxane solvent mixtures were determined spectrophotometrically. Furthermore, the acidity constants (pKa) of bromocresol purple in binary aqueous-dioxane at constant ionic strength 0.5 mol.dm^{-3} potassium chloride and at room temperature ~25°C was analyzed in relevance physicochemical parameters of water-dioxane solvent characterizing its non-electrostatic and electrostatic interactions with the solute.

EXPERIMENTAL

Materials and preparation of solutions

The bromocresol purple, and reagents utilized during this work were purchased from Merck, BDH and Fluka companies. All chemical and reagents were of analytical grade and used without further purification.

The universal buffer was prepared by blending 0.04 mol.dm^{-3} of boric, phosphoric and glacial acetic acids and including the specified volume of 0.2 mol. dm^{-3} sodium hydroxide (CO_2-free) to grant the desired pH. The ionic strength of the considered solution was balanced by including 0.5 mol.dm^{-3} solution of potassium chloride. All solutions were prepared with de-ionized and CO_2-free water.

Stock solutions (1.85×10^{-3} mol.dm^{-3}) of the bromocresol purple were prepared by dissolving a known mass of the solid within the required volume of binary mixtures from water-dioxane solvent in ratios 0, 30, 40, 50, 60 and 70 % (v/v). The pH control was achieved modified universal buffer solutions [8].

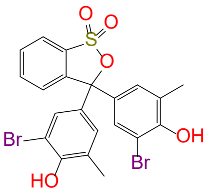

Fig.1. Structure of bromocresol purple (BCP).

Instrumentations

The electronic absorption spectra were recorded on CECIL-CE 7400 (S.n.146368, England) UV-Visible Spectrophotometer model cell, using 1 cm matched quartz cells within the wavelength range of 250 nm - 750 nm. The pH measurements were carried out using precise pH-benchmeter Model PHS-3C accurate to ± 0.01 pH unit, where the pH meter is standardized using aqueous buffers at room temperature ~25°C.

Calculation of acidity constants from spectrophotometric data

The acidity constants of the bromocresol purple were calculated by using of the data obtained within the pH range 2 - 12. Two approaches were applied to evaluate the acidity constants from spectrophotometric data [16].

The half-curve height method

The pK is evaluated at a constant wavelength from the half height of the A_S versus pH curves as follows:

$$pH = pK + \log \frac{(As)_{1/2}}{(As)_{max} - (As)_{1/2}} + \log \gamma$$

where γ - activity coefficient terms and controlled by ionic strength of supporting electrolyte, at $(A_S)_{1/2} = ½ (A_S)_{max}$ then $\frac{(As)_{1/2}}{(As)_{max} - (As)_{1/2}} = 1$.

The pKa values were calculated from half height of the curve which, pKa = pH, Fig. 2(b).

The modified limiting absorbance method

In this method, the pKa values were evaluated by applying the subsequent equation:

$$pH = pKa + \log\gamma + \log \frac{A - A_{min}}{A_{max} - A}$$

where A_{max} is that the maximum absorbance, A_{min} is that the minimum absorbance, A is that the absorbance at any pH and γ is activity coefficient term, by plotting the log absorbance ratio versus pH. The line should have a slope, the values of slope and correlation coefficients are shown in Table 1.

RESULTS AND DISCUSSION

Electronic absorption spectra in universal buffer solutions

Bromocresol purple is colored yellow at pH = 2 - 3 and greenish-yellow at pH = 4 - 5 and blue-purple at pH = 6 - 7 and it changes to violet at pH ≥ 8. The change from a violet to yellow color of the molecule following the decrease of pH is associated to the modification of the π system delocalization pattern [16]. The proton dissociation scheme can be represented as below:

$$H_2In \overset{pKa1}{\longleftrightarrow} HIn^- \overset{pKa2}{\longleftrightarrow} In^{-2}$$

The electronic spectra of bromocresol purple (1.85×10^{-5} mol.dm^{-3}) solution in different proportions of dioxane aprotic solvent, (50 % (v/v) water-dioxane solution), within the pH range (2 - 12) as for instance, Fig. 2(a), The spectrum for solutions of pH ≥ 6 is characterized by three absorption bands centered at 295 nm (π-π*); at 380 nm (n-π* of OH group) [3] and at 590 nm (n-π* assigned to CT nature formed through the conjugation between the aromatic rings systems via the C atom link). On increasing the pH of the medium, the intensity of the latter band is increased due to formation of In^{-2}, Fig. 3(III). The fine isosbestic points around 315 nm and 490 nm points bent the existence of acid-base equilibrium, with as possible different structures [17]. For acidic solutions of (pH ≤ 5) showed the band centered at 430 nm, this band disappeared with increasing the pH of the medium as result formation In$^-$, Fig. 3(II). The sample of distribution diagrams for bromocresol purple species in several water-dioxane mixtures is shown in Fig. 4. The variation of the species is due to the acid dissociation shifting as pH changes. [18]

The values of calculated pKa for bromocresol purple in various volume fractions of water and dioxane are listed in Table 1. Calculations at 590 nm using the two mentioned spectrophotometric approach's, reveal two pKa's, Fig. 3. The pKa$_1$ value, Fig. 3(II), is attributed to the dissociation of the sulphonic group of the neutral variety of H_2In, Fig. 3(I), which is completely dissociated

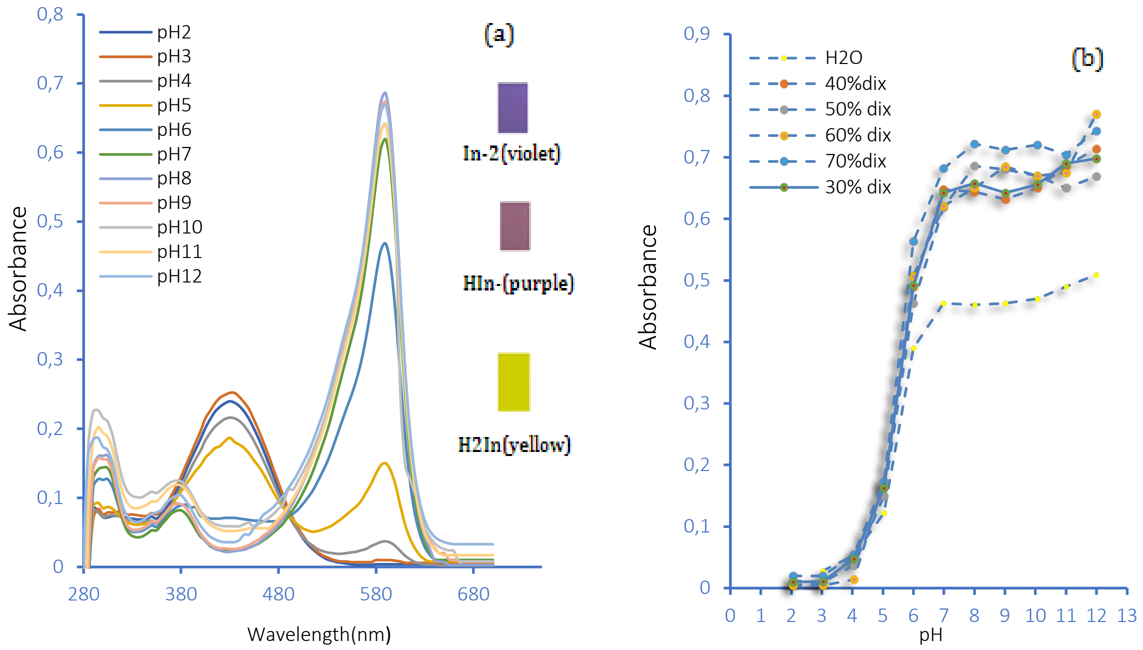

Fig. 2. (a) the electronic absorption spectrum of 1.85×10^{-5} mol.dm^{-3} solution of BCP in 50 % water-dioxane at different universal buffer pH's; (b) the half height method; absorbance versus pH curve of BCP at λ_{max} = 590 nm in pure water and different proportion of dioxane.

Table 1. Dissociation constants of bromocresol purple in numerous binary solutions of water and dioxane (at 590nm) at room temperature ~25°C, and constant ionic strength 0.5 mol.dm^{-3}KCl.

% dioxane	Method 1		Method 2		Average		slope		R		Ref.
	pka_1	pka_2	pka_1	pka_2	pka_1	pka_2	pka_1	pka_2	pka_1	pka_2	
0.00	5.45	10.70	5.49	10.97	5.47 ± 0.03	10.84 ± 0.15	0.70	0.88	0.962	0.999	this work
30	5.48	11.15	5.40	10.94	5.44 ± 0.06	11.05 ± 0.15	1.12	0.65	0.992	0.950	this work
40	5.45	11.20	5.32	11.32	5.39 ± 0.09	11.26 ± 0.08	0.95	1.15	0.938	0.972	this work
50	5.40	11.40	5.29	11.35	5.35 ± 0.08	11.38 ± 0.04	0.99	0.25	0.985	0.581	this work
60	5.38	11.45	5.27	11.51	5.33 ± 0.08	11.48 ± 0.04	0.98	0.39	0.977	0.689	this work
70	5.30	11.60	5.14	11.42	5.22 ± 0.11	11.51 ± 0.13	0.66	0.30	0.936	0.499	this work
0.00					5.4						21
0.00					6.4^a	11.64^b					22

**the slope value and correlation coefficient (R) are from method 2, a: H_2O, b: isopropyl*

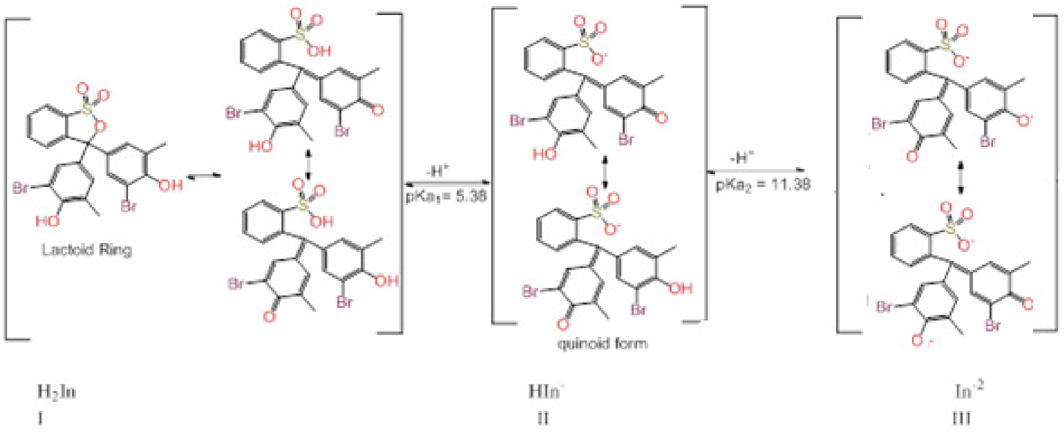

Fig. 3. The dissociation mechanism of bromocresol purple.

[19]. However, the pKa_2 value is attributed to the dissociation of the OH group from the shape HIn^-, Fig. 3(III), this pKa is usually [20] around ten. The phenol acidity is increased by reduce the electronic density of the O-H bond, since the aromatic ring bound to OH reduces its electronic density by resonance although bromine has a smaller electronegativity. The electron withdrawing effect of bromine is countered by the electron donating methyl group so, the net to electron withdrawing effect is small and it causes ionization of OH with pKa values above 10.

The above findings clarify the pKa_2 value is influenced by the inductive effect of the substituent besides others factors. This fact is confirmed by the obtained acidity constant of bromocresol purple in pure water (pKa_2 = 10.84) in pH range 9 - 12 at (0.5 mol.dm^{-3} KCl, ~25°C, Table 1). Therefore, the first pKa_1 = 5.47 value in pure water within the range 2 - 8 is analogous to this reported within the literature [21] (pKa_1 = 5.4) at the same temperature but is different with value listed by Barbosa [22]. These small differences are due to the different experimental method used to estimate the

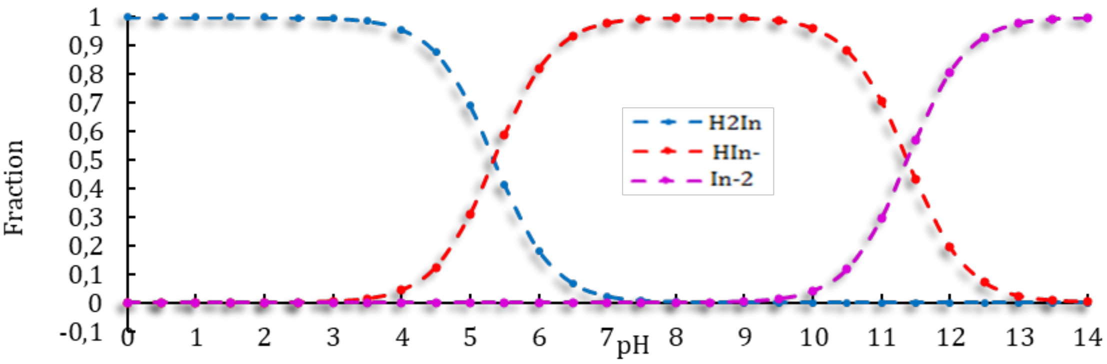

Fig. 4. Distribution diagram of the acid species of bromocresol purple indicator in % 50 (v/v) water-dioxane at various pH's.

values. Therefore, these variations are due to of different experimental conditions of solvents, temperature, dye concentration, ionic strength, pH range, methods of analysis, analyzed wavelength range, and the self-aggregation tendency of indicator in water [21 - 23].

The influence of solvent on the acidity constants

The data shown in Table 1 sincerely illustrate the important influence the character of solvent on the dissociation reactions discussed in the solvating ability term [24]. Water can dissociate the acid and stabilize the produced anion and hydrogen ion because the water have high solvating ability (i.e. donor number DN = 33.0) and relative permittivity ($\varepsilon = 78$). The dependence of the acidity constants of bromocresol purple on the solvent composition is due to the preferential solvation of the charged particles mainly by water.

Examination of the results depicted in Table 1 reveals that the pKa_1 values in the presence of the poorer hydrogen-bond donor dioxane are decreased with increasing of amount of dioxane solvent. This behavior is often ascribed to the high basic property of dioxane, which reflects itself in the construction of a strong hydrogen-bond acceptor from the SO_3H group of the non-ionized indicator molecule and consequently promotes the ionization process (i.e., low pKa). The dispersive interaction between the delocalized charge on the conjugated base of the indicator (HIn^-) and also the localized dispersion centers in near solvent molecules, which possibly exist within the media used, in addition, the proton-solvent interactions have important effects on the ionization process of the indicator studied, with increasing the amount of cosolvent both (HIn^-) and H^+ will be highly stabilized by dioxane molecules [25]. Therefore, the rise in the pKa_2 with increasing the mole fraction of dioxane in the binary mixtures is due to the solute-solvent interaction of the various species within the mixtures. It indicates also that the difference within the stabilization of the ionic forms, by hydrogen-bond basicity solvent molecules plays an essential role in the rise of the pKa_2 values as the amount of the dioxane in the medium is increased. Since water molecules have a higher tendency to donate hydrogen-bonds than dioxane solvent molecules therefore, in absence of specific interaction between the acid and solvent, pKa should be linear function. This is caused by a change in the free energy of solvation of both the non-ionized and their ionized species in going from aqueous to aqueous dioxane solutions.

The dissociation of an uncharged acid (H_2In, Fig. 3(I)) in a solvent requires the separation of two ions of opposite charges. The energy required for dissociation is supplied by solvation of the ions, and also the proton transfer from acid to the solvent molecule supplies an extra energy. This finding indicates that other solvent effects beside the electrostatic one have a contribution to the ionization process of the investigated indicator. This fact is further substantiated by the nonlinear relations obtained by plotting of pKa against $1/\varepsilon$ of the medium Fig. 5, therefore, the equation given by Denison, Ramesy and Gilkerson which relates the variation of the pKa of the acid with the relative permittivity of the medium ε, which the relative permittivity of aqueous mixtures, ε, was obtained using the subsequent equation [26].

$$\varepsilon = \varepsilon_1 x_{(W)} + \varepsilon_2 x_{(S)}$$

where ε is the relative permittivity of aqueous mixtures, ε_1 and ε_2 are the relative permittivity of the water and organic solvent, respectively; x is that the mole fraction,

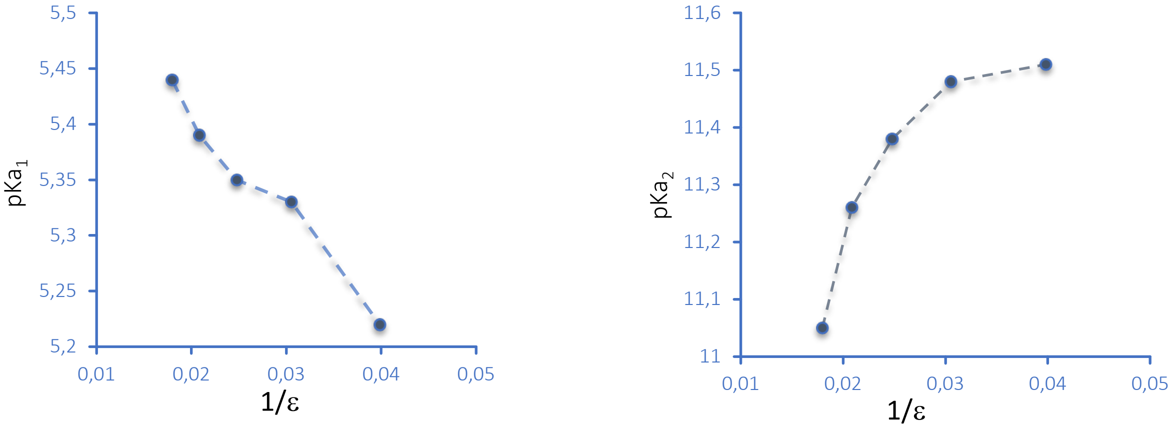

Fig. 5. Variation of pKa of 1.85 × 10^{-5} mol.dm^{-3} solution of bromocresol purple in water-dioxane mixtures with 1/ε of the medium at room temperature.

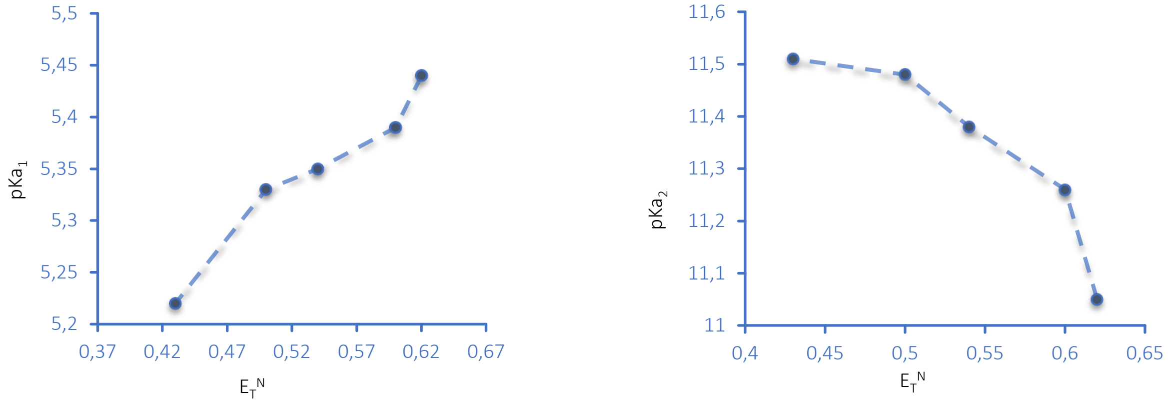

Fig. 6. Plot of p*K*a of bromocresol purple vs. the Dimroth-Reichardt parameter E_T^N of water-dioxane mixtures.

and therefore the subscripts w and s consult water and organic solvent, respectively. In general, effects like hydrogen bonding solvent basicity, dispersive forces, and proton solvent interactions play vital roles within the ionization process of acids within the presence of organic solvents.

Fig. 6 shows the plot of p*K*a values of bromocresol purple vs. the Dimroth-Reichardt parameter E_T^N reflecting the electron acceptor power (acidity) of water-dioxane blends [27]. These plots show that, with increasing E_T^N, the first acid dissociation constants pKa_1 of bromocresol purple increase nonlinearly, in contrast, the second dissociation constant pKa_2 is decreased nonlinearly. These results suggest that bromocresol purple is solvated in water - dioxane mixtures due to both specific and nonspecific interactions with the solvent molecules.

The multimode solvation of bromocresol purple in water-dioxane mixtures is confirmed by the fact that p*K*a values of bromocresol purple may be a linear function of the dioxane mole fraction in water-dioxane mixtures with correlation coefficient 0.929 and 0.925, respectively, Fig. 7. These correlations show that the bromocresol purple under consideration is similarly solvated with water and dioxane molecules in water-dioxane solvent blends [28].

The correlation of acidity constants with Kamlet-Taft parameters

The tactic of Linear solvation energies relationship (LSER) should be because the most successful among the multiparametric quantitative methods [29], which uses empirical solvatochromic parameters of solvent polarity α, β, and π* introduced by Kamlet and Taft and

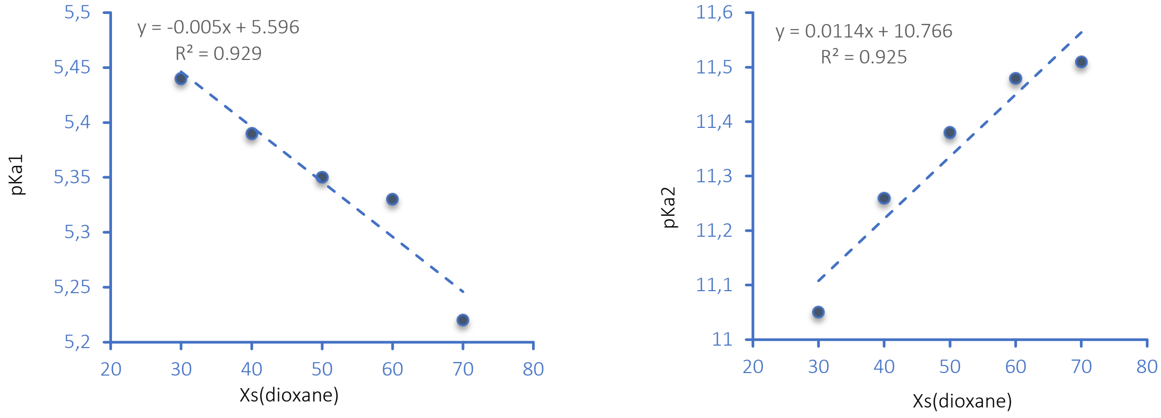

Fig. 7. Plot of p*K*a values of bromocresol purple vs. the dioxane mole fraction in water-dioxane mixtures.

Table 2. Regression coefficients of the KAT equation for pKa's values of bromocresol purple in different Water-dioxane mixture**s.**

% $_{\text{Dioxane}}$	Solvent Parameters				Coefficients	pKa_1	pKa_2
	α	β	π*	E_T^N	constant	5.10(0.16)	7.43(0.23)
0	1.17	0.47	1.14	1.00	a	1.32(0.09)	-0.35(0.13)
30	0.82	0.56	1.05	0.62	b	-0.52(0.21)	6.58(0.31)
40	0.77	0.59	0.99	0.60	s	-0.43(0.44)	0.22(0.064)
50	0.73	0.61	0.92	0.54	R	0.999	1.000
60	0.60	0.63	0.55	0.50	F	326.14	795.92
70	0.52	0.63	0.56	0.43	OSD	0.005	0.008

E_T^N :Dimroth-Reichardt parameter, β :basicity , α: acidity , π: dipolarity /polarizability , (a, b and s): regression coefficients, R: correlation coefficients, F: Fisher number; OSD: overall standard deviation

characterizing, respectively, the ability of the solvent to act as the hydrogen bond donor (acidity) or acceptor (basicity), and ability of the solvent to nonspecific interactions (relative permittivity/polarizability). The Kamlet-Taft formalism is widely used in various studies to describe the effect of environment on the protolytic properties of solutes in non-aqueous and mixed solvents, including water-aprotic solvent mixtures [30 - 32]. Within the latter case the Kamlet-Taft equation is represented as:

$$pKa = pKa_o + a\alpha + b\beta + s(\pi* + \delta) \qquad (1)$$

where pKa_0 is the acidity constant in an environment with zero values of α, β, and π* (e.g., cyclohexane), *s*, *a*, and *b* are the coefficients taking into account the contributions of the respective sorts of interactions in the overall effect of the medium.

To explain the effect of solvent on dissociation constants of BCP based on the KAT solvent parameters, pKa_1 and pKa_2 values were correlated with solvent properties by means of multiple linear regressions analysis in SPSS program. All of single, dual and multi-parametric fitted equations were considered. However, the number of parameters in the equation depends on the significance of the solute-solvent interactions. The F-statistic values were used to assess which of the LSER equations is statistically optimum model. The best predictive mathematical equation in the fitted models was obtained according to the highest F-statistic and smallest standard deviation values. The KAT parameter values for aqueous-dioxane mixtures used in this work were obtained from the values reported in the literature and are listed in Table 2 [33]. The most significant resulting regression equations describing the correlation between acidity constants of bromocresol purple and the KAT parameters are shown in Table 2.

R^2 and F are squared correlation coefficient and F-statistic values, respectively. The number in bracket shows the standard deviation of each regression coefficient. The multi-parameters coefficients within Kamlet-Taft equation are ordered in Table 2, the results showed that the positive sign of the (a coefficient) for pKa_1 in water-dioxane blends, which suggests that decrease in the acidity with increasing mole fraction of dioxane cause decrease of the pKa_1magnitueds. Thus, α has major role for the system [34] compared to basicity of solvent, the rational for this phenomenon may be a significant difference within the preferential solvation effects of the studied indicator. However, negative sign of (s coefficient) indicates that a decrease in the polarity of the media increases the dissociation constants. This result indicates that the dissociation of BCP is mainly dependent on specific solute-solvent interactions in water-dioxane mixtures. The correlation analysis of $pKa_{2,}$ the positive (s and b coefficients) indicate that decrease within the polarity or arise within the hydrogen bond acceptor basicity parameters of the solvent blends that causes the dissociation constants values increases. The dissociation process in water-dioxane is governed by Hydrogen bond acidity and basicity (solvation effects). However, α has negative value; indicating the increase of dissociation constant with decreasing acidity of the solvent. The observed different solvent effect on different regions may relate to the structural change of binary mixtures due to solvent-solvent interactions and possibility of preferential solvation [35].

CONCLUSIONS

In this work, we investigate the behavior of acidity constants of bromocresol purple in pure water and in water with dioxane containing 30, 40, 50, 60, 70 % (v/v) at ~25°C and constant ionic strength 0.5 $mol.dm^{-3}$ potassium chloride and were studied by spectrophotometric method. Results show that the pKa values are changed as the percentage of dioxane increasing. Although the polarity of media decreases with increasing dioxane in solution. This result confirmed by the non-linearity obtained from the relation between the acidity constants and $1/\varepsilon$, this result indicates that both non-specific and specific solute-solvent interactions affecting on the acidity constants of bromocresol purple. From this result the data was analyzed in terms of Kamlet-Taft equation by using linear solvation energy relationship concept. The results show the hydrogen ability have more impact on the acidity constants with different values, the hydrogen bond acidity has more impact than the hydrogen bond basicity in case the pKa_1 and vice versa in case the pKa_2 due to preferential solvation by water and dioxane molecules in all ratio with different effect related to the structure change of binary mixtures.

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