

The Electrostatic and Non-Electrostatic Interaction Affect on Acidity Constants of Bromocresol Purple in Aqueous Ethanolic Media

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Abstract

This work aimed to study the effect of ethanol ratios on the acidity constants of bromocresol purple. The acidity constants of BCP were determined in binary mixtures of water with ethanol containing 0, 30, 40, 50, 60, and 70% (v/v) using spectrophotometric methods. The results indicate the dependence of acidity constants on the ratio of ethanol. The values of $\log K_{a1}$ and $\log K_{a2}$ were correlated with the macroscopic (relative permittivity, ϵ) and microscopic Kamlet-Taft parameters (α , β , and π^*) of binary mixtures. The influence of solvent on the acidity constants was analyzed in terms of the KAT parameters in order to study the solvent-solute interaction. Multiple linear regression was used to find the contribution of the microscopic parameters containing α (acidity), π^* (dipolarity/polarizability), and β (basicity). It was found that α and β were the most predominant descriptors. Also, a relationship with reciprocal relative permittivity was obtained based on Born's model, showing the significance of specific solute-solvent interactions. Therefore, the hydrogen bonding interactions between solute and solvent components are mainly responsible for the change in acidity constants of bromocresol purple of binary mixtures.

Introduction

The acidity constants are essential parameters that refer to the dissociation of molecules in solution under various pH values. The acidity constants of compounds play a necessary role in numerous analytical techniques like neutralization titration, solvent extraction, complex formation, ion transfer, and many other analytical procedures. Many of the theoretical principles of recent chemistry are based on observing the impacts on chemical equilibria of various structures.¹⁻³ Many techniques are applied to estimate the acidity constants, including potentiometric titration, spectrophotometric determination, and conductometry.⁴

The spectrophotometric technique is more sensitive and appropriate for studying solution chemical equilibria. For various acid-base indicators, which have different functional groups, there is a marked spectral change with the pH variation of the solution.⁵⁻⁷ The electronic spectral data are used to calculate the acidity constant of the indicators under investigation. The values of the acidity constant are estimated at 25°C by the dependence between the optical density and thus $-\log [H^+]$. Therefore, acidity constant values provide a basis for understanding the chemical reactions between two molecules in solutions. In addition, the acidity constants are used to detect the structure of a new substance.⁸

Mixtures of aqueous solvents from methanol and ethanol are widely used due to the weak solubility of the various compounds in pure water.^{9,10} Further, changing the contents of solvent in the mixture give a solvent with new properties, both physical such as permittivity, and chemical, such as acid-base properties. Thus, the acid-base property is an important property of solvents based on the strength of acids and bases. Therefore, the medium's polarity and relative permittivity causes differences in the strength of dissolved acids and bases due to the selective preferential solvation of both acid and conjugated base.¹¹ The degree of ionization of solute is based on the relative permittivity of the solvent. The media of higher relative permittivity strongly dissociate, whereas those of low permittivity ionize to a lesser extent¹². Understanding the impact of solvents on the dissociation equilibria was achieved by electrostatic interactions (Born model).¹³ Consequently, recent studies have revealed that the variation in macroscopic properties, such as the relative permittivity of the solvent, cannot be the only factor.¹⁴

Bromocresol purple (BCP), Fig. 1, is used as a pH indicator, colored yellow at a pH lower than 5.2 and violet at a pH higher than 6.8,¹⁵ this change in color at a specific pH due to delocalization of the π system is produced variety

resonance structures, thus, which occurs via proton exchange from BCP into H₂O or vice versa, which bromocresol purple exists in two main forms in aqueous solutions.^{16, 17}

In this study, the acidity constants of bromocresol purple were estimated in numerous volume fractions of water and ethanol. In addition, the dependence of acid-base equilibria on solvent contents was examined. Furthermore, the acidity constants of bromocresol purple in binary water mixtures with ethanol at room temperature were analyzed using a linear solvation energy relationship.

Experimental

Materials and preparations of the solutions

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

The universal buffer utilized in this work was prepared by mixing 0.04 M of boric acid, phosphoric acid, and glacial acetic acid and including the necessary volume of 0.2 M NaOH to grant the required pH. In addition, the ionic strength of the considered solution was balanced by including a 0.5 M solution of KCl. All solutions were prepared with deionized and CO₂-free water.

Stock solutions (1.85×10⁻³ M) of bromocresol purple were prepared by dissolving the appropriate amount (25 mg) in the required volume of the binary mixture and diluted to 25 mL with aqueous ethanol in the ratios 0, 30, 40, 50, 60, and 70% (v/v). The pH control was achieved using modified universal buffer solutions.⁸

Instrumentations

The electronic absorption spectra were measured using CECIL-CE 7400 UV-Visible Spectrophotometer within the wavelength range of 250–750 nm using matched cells of 1 cm path length. The pH measurements were carried out using precise pH-benchmark Model PHS-3C accurate to ± 0.01 pH unit, where the pH meter was standardized with standard buffer solutions (pH = 7 and 10) at ~ 25°C.

Calculation of acidity constants from spectrophotometric data

The acidity constants of bromocresol purple were calculated using the data obtained in the pH range of 2–12, in which two approaches were applied to estimate the acidity constants.¹⁸ These approaches include the half-curve height and the modified absorbance methods.

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:

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

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

$$\frac{(A_S)_{1/2}}{(A_S)_{\max} - (A_S)_{1/2}} = 1.$$

then The pKa values are calculated from the half height of the curve where pKa = pH.

The modified absorbance method:

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

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

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

Results And Discussion

The impact of buffer solutions on the electronic spectrum of bromocresol purple.

Bromocresol purple is an acid-base indicator with a 90% content of dye. It is colored yellow at pH = 2–3, greenish-yellow at pH = 4–5, and blue-purple at pH = 6–7, and it changes to violet at pH \geq 8. The UV-Vis spectrum of ($1.85 \cdot 10^{-5}$ M) bromocresol purple in aqueous ethanol at various pH values was recorded. Sample of this spectrum at different pH values within the pH range (2–12) in aqueous ethanol mixtures are shown in Fig. 2. The spectrum for solutions of pH \geq 6 is represented by three absorption bands focused at $\lambda_{\max} = 305$ nm is attributed to π - π^* transition of the benzenoid system present in their structure^{6,7}; at $\lambda_{\max} = 380$ nm is assigned to n- π^* transition of OH group⁷ and at $\lambda_{\max} = 590$ nm (n- π^* is assigned to CT nature due to the conjugation between the aromatic rings systems via the C atom link)⁶. Therefore, on increasing the medium's pH, the latter band's optical density ($\lambda_{\max} = 590$ nm) gradually grows due to the formation of BCP⁻², Fig. 3 III. The acidic solutions (pH \leq 5) showed a band centered at 430 nm; this band disappeared with increasing the pH of the medium as a result formation of HBCP⁻ in accordance with results in literature¹⁹, Fig. 3 II. The first band centered at $\lambda_{\max} = 305$ nm is shifted to a higher wavelength with decreasing the pH of the medium. Therefore, the change in color from violet to yellow of the compound with decreasing pH is attributed to the delocalization of the π system.²⁰ The presence of fine isosbestic points at around 315 and 490 nm indicated the presence of acid-base equilibrium, with as possible different structures²¹, Fig. 3. The sample of distribution diagrams for bromocresol purple species in various binary mixtures of water with ethanol are shown in Fig. 4. The variation of the species is due to the acid dissociation shifting as pH changes.⁷

The calculated values of acidity constants (logKa) for bromocresol purple in various binary mixtures of water with ethanol are listed in Table 1. Calculations at $\lambda_{\max} = 590$ nm using the two mentioned spectrophotometric approaches reveal two pKas. The logKa₁ value, Fig. 3II, is assigned to the ionization of the sulphonic group⁷ from the neutral kind of H₂BCP (Fig. 3I) because the sulphonic group is completely dissociated.²² The dissociation phenolic hydrogen group from the indicator form, Fig. 3 III, logKa₂ in general, this pKa has a value around ten.²³ In this work, the obtained acidity constants in pure water agreed with those reported previously, Table 1. The first pka₁ is 5.47 in the pH range 2–8; this pKa is similar to the reported in literature²⁴ while is different from the value reported by Barbosa,²⁵ in which a small difference is attributed to the different experimental approach used to estimate the pKa values. In

contrast, the second pK_{a2} in pure water is above ten due to the inductive effect for substituents besides other factors affecting it. Moreover, these variations attributed to the various experimental settings, including intensity of heat, dye amount, pH extent, ionic strength, techniques of analysis, analyzed wavelength extent, and the BCP self-association ability in the water, are affected by the values of acidity constants²⁴⁻²⁶.

Solvent effect

On a scrutiny of the results in Table 1, one notices that the acidity constants of bromocresol purple $\log k_{a1}$ and $\log k_{a2}$ gradually grow with increasing ethanol percentages in binary mixtures. This fact can be explained by the change in solvent properties.¹¹ since ethanol species in the water-rich region occupy the spaces between the water molecules without disordered the water structure.²⁷ In contrast, in the ethanol-rich region, the bromocresol purple molecules are surrounded by the ethanol and water species.^{27,28} This variation in the percentage of the ethanol solvent is due to solute-solvent and solvent-solvent interaction effects. Intermolecular forces between the solution components can influence solvent-solvent interactions. This effect possibly changes the structure of the mixtures when the percentage of the organic solvents increases to higher values.²⁸ This discussion follows previous results for other aqueous-organic solvent mixtures and agrees with the present results.²⁹

Effect of solvent parameters on acidity constants of bromocresol purple

To clarify the dissimilarity of the values of acidity constant for a molecule own to the ethanol ratio in the mixtures using the relative permittivity of the solutions as the only factor is very difficult. Generally, the standard Gibbs free energy of dissociation equilibrium includes two parts: an electrostatic part, which can be evaluated by the born equation and a non-electrostatic part which involves specific interaction between solute and solvent.³⁰ In case, the electrostatic effects predominate on non-electrostatic effect, so the graph of pK_a 's against the reciprocal of relative permittivity of the medium, ϵ , gives a linear correlation assigned to the born model (Eq. 1),

$$\Delta \log K_a = \left(\frac{121.6n}{r} \right) \left(\frac{1}{\epsilon} - 0.0128 \right) \dots (1)$$

Where r is the ionic radius and n is the square summation of the charges; $\log K_{a1}$ and $\log K_{a2}$, the linear relationship was obtained with reciprocal of the relative permittivity of ethanol blends (with correlation coefficient 0.94 and 0.93 respectively), where the values of relative permittivity are obtained from³¹, Fig. 5. The slope of plots is related to the term n in Eq. 1. For first and second acid-base equilibria, n is -5 and -10, respectively. A negative sign of n indicates that species on the left-hand side of reactions are more polar than those on the other side.³⁰ Therefore, this result indicates that BCP dissociation was dependent on the electrostatic interactions and strongly depended on the specific solute-solvent and solvent-solvent^{29,30}. The ϵ can show the power of interaction between species in a solution.

To estimate the influence of solute-solvent interaction on the acidity constants. The Kamlet, Abboud, and Taft (KAT) were used³² (Eq. 2) to describe the solvent effect and solute-solvent interaction based on the linear solvation energy relationship. This equation includes electrostatic and non-electrostatic interactions separately. The partition of non-electrostatic interaction into solvent acidity interactions (HBA solute-HBD solvent) and solvent basicity interactions

(HBD solute-HBA solvent). In contrast, all of these parameters reflect each intermolecular force that occurs between solute and solvent species because it measures the solvent polarity rather than the relative permittivity or other uni-parameter. Universal, this strategy has been vastly used in the relationship analysis of all kinds of solvent-dependent processes¹⁵. Multi-parametric strategy (Eq. 2) is used with the solvatochromic solvent parameters, α , β and π^* , which are reported previously^{31,33-36}.

$$\log K_a = \log K_{a_0} + a\alpha + b\beta + s\pi^* \dots (2)$$

Where $\log K_a$ represents the regression value, the Kamlet-Taft solvent parameters (π^* , α , β) determine the dipolarity/polarizability, the acidity strength, and the basicity strength of the solvent. The regression coefficients a , b , and s are the parameters properties of the solute. Their values and sign define the impact of solute-solvent interactions on the acidity constants of bromocresol purple.

To explain the acidity constants magnitudes by the KAT strategy, the acidity constants were analyzed with the solvent terms using single, dual, and multiple regression analysis using the IBM-SPSS program.

The technique that is used in the regression analysis involves accurate statistical treatment to pick up which term in Eq. 2 is the best fit for aqueous ethanol mixtures; hence, a stepwise technique and least-squares analysis are applied to pick out the significant solvent characteristic to be impacted in the strategy and to extract the last formula for the acidity constants. In universal, the KAT model, Eq. 2, is minimized to single, dual, and multi-parameters for relation analysis of $\log K_a$ in different ethanol blends. The SPSS program can create the magnitudes of $\log K_{a_0}$, a , b , s , and some statistical terms involving the r^2 regression factor, f-test (f), the residual sum of squares (RSS), the standard deviation of any term and the overall standard error (OSE) of $\log K_a$. For each studied solution in this work, the KAT parameters for the binary mixtures used were taken from Marcus et al.³⁷ and are reported in Table 2.

Table 1

Dissociation constants of bromocresol purple in numerous binary Solutions of water and ethanol at ~25°C, ionic strength 0.5M KCl.

%EtOH	Method ₁		Method ₂		Average		Slope		R		Ref.
	logka ₁	logka ₂	logka ₁	logka ₂	logka ₁	logka ₂	logka ₁	logka ₂	logka ₁	logka 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	5.50	11.20	5.49	10.93	5.49 ± 0.01	11.06 ± 0.21	0.99	0.32	0.998	0.458	
40	5.50	11.25	5.49	10.90	5.50 ± 0.01	11.08 ± 0.25	0.99	0.83	0.977	0.834	
50	5.55	11.45	5.50	10.80	5.52 ± 0.04	11.13 ± 0.46	0.99	0.84	0.995	0.781	
60	5.60	11.50	5.53	11.02	5.57 ± 0.05	11.26 ± 0.34	1.07	0.59	0.999	0.947	
70	5.65	11.55	5.58	11.52	5.62 ± 0.05	11.54 ± 0.02	1.02	1.98	0.998	0.999	
0.00					5.40						
0.00					6.4 ^a	11.64 ^b					25
Where the slope and correlation coefficient(R) from method 2, a: H ₂ O, b: isopropyl, Ref.: reference.											

Although the solvent polarity is an essential factor in the change of logKa magnitudes in various aqueous ethanol blends, the results with any single-parameter correlations of logKa₁ and logKa₂ magnitudes individually with π^* , α , and β did not give appropriate results in all cases with lower of F-static. However, the correlation analyses of logKa₁ and logKa₂ magnitudes with multi-term equations become more pronounced with minimum overall standard deviation) corresponding to the single- or dual-term strategies. The expressions of the KAT model for each property are obtained and given as multi-term as follows; the standard deviation magnitudes for each term are shown inside the bracket using the SPSS program, see Table 2. The parameters of α , β and π^* in Table 2 are different the positive value of β term in the correlation analysis of the multi-term of the KAT equation in the case of logka₁ ($\beta > \alpha > \pi^*$) and has a much more pronounced for system and the polarity term are significantly lower than the hydrogen ability. So, logka₁ values growth with the rise in hydrogen bond basicity term. Correlation analysis of (the negative s and negative a) coefficients indicate that the rise in the polarity and the acidity terms of the ethanol blends causes a decrease in the constant acidity values.

Table 2

Solvent parameters and KAT regression coefficients for logKa's values of bromocresol purple in various water-ethanol blends.

% EtOH	Solvent Parameters				Coefficients	logKa ₁	logKa ₂
	α	β	π^*	ϵ	constant	5.72 (0.59)	18.73 (1.48)
0	1.17	0.47	1.14	78.90	a	-1.81(0.39)	-12.28(0.99)
30	0.96	0.66	0.99	66.00	b	2.75 (0.52)	7.37 (1.30)
40	0.96	0.65	0.88	59.60	s	-0.30(0.03)	-0.746(0.07)
50	0.96	0.65	0.79	55.00	R	0.999	0.999
60	0.96	0.66	0.73	47.50	F	148.543	316.840
70	0.94	0.66	0.68	41.10	OSD	0.0051	0.0128
					RSS	$2.6 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$
					P	0.060	0041
Where ϵ : relative permittivity, β : basicity, α : acidity, π : dipolarity /polarizability, (a, b and s): regression coefficients, R: correlation factor, F: f-test; P: the probability of variation, OSD: overall standard deviation, RSS: the residual sum of squares							

On scrutiny of the results in Table 2, the correlation analysis of logKa₂ shows that the acidity parameter has a more impact with a negative value; this suggests that the rise in hydrogen donating ability of the medium causes a decrease in acidity constant. The observed solvent effects on different regions may relate to the structural change of binary mixtures due to solvent-solvent interactions and the possibility of preferential solvation²⁹. Moreover, the negative value of α indicates that a decrease in the HBD ability of the mixed solvents leads to increased solubility of the formed anions. Consequently, the acidity constants grew when this term lowered.

In other words, negative values for this parameter are observed in most cases due to donor-acceptor interactions with a solvent, causing a displacement in the acid-base equilibrium towards phenolate anions due to the energy stabilization (Gibbs energy decrease).³⁸

From Table 2, the negative sign of the s coefficient is attributed to a decrease in the polarity of the mixed solvents, causing increases in the logKa₁ and logKa₂ values. Thus, the rise in the polarity leads to increases in the solubility of the particles, and thus dissociation equilibrium becomes more likely. Finally, the negative sign of the s term, which is consistent with the idea of the influence of the dielectric constant on the acidity constant in accordance with the Born model, is often in good agreement with the results reported by Shorina and co-worker.³⁹

Conclusions

The acidity constants of bromocresol purple were determined in binary mixtures of water with ethanol at constant ionic strength. The relationship between acidity constants and relative permittivity as a macroscopic term or KAT solvatochromic parameters as microscopic terms was evaluated. Although the polarity of media decreases with increasing ethanol in solution, Born's model examination indicates that the non-specific electrostatic solute-solvent interactions have a doubtful effect on the acidity constants of BCP. Based on the results of Born's model, the data were analyzed in the KAT multi-term regressions using a linear solvation energy relationship. The results showed that

non-electrostatic (specific) is more significant than electrostatic (non-specific) on acidity constants with different values resulting from preferential solvation with water-ethanol aggregates in all binary mixtures.

Declarations

Conflict of interest statement

The authors declare no conflict of interest.

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Figures

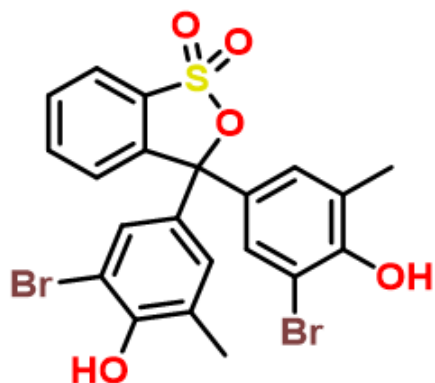


Figure 1

The chemical structure of bromocresol purple (BCP).

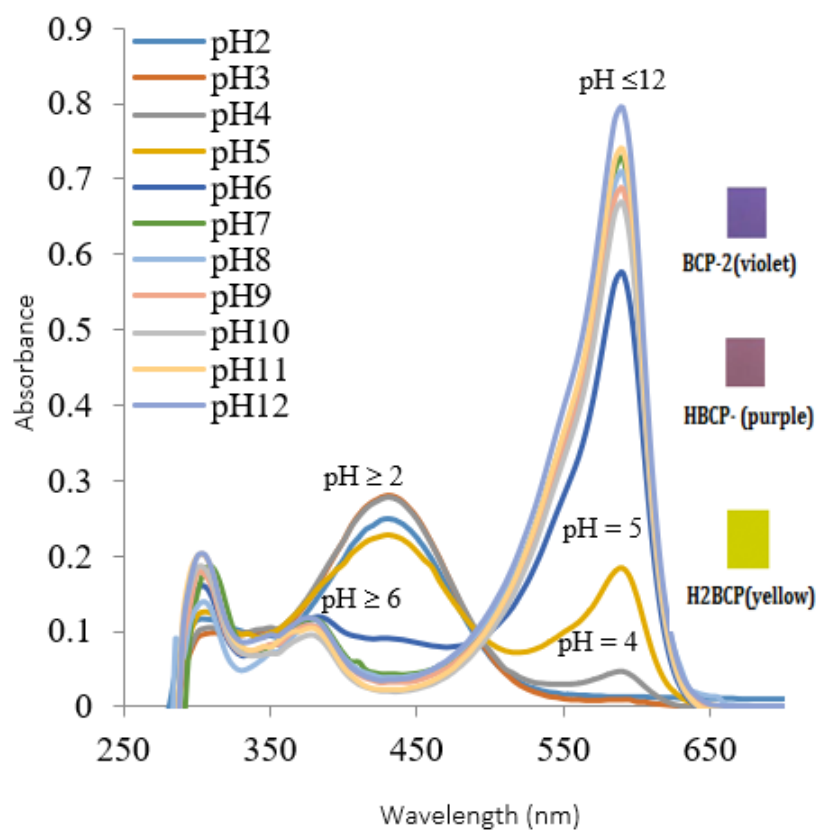


Figure 2

The electronic absorption spectrum of 1.85×10^{-5} M of BCP in (50 % aqueous ethanol) at different pH's.

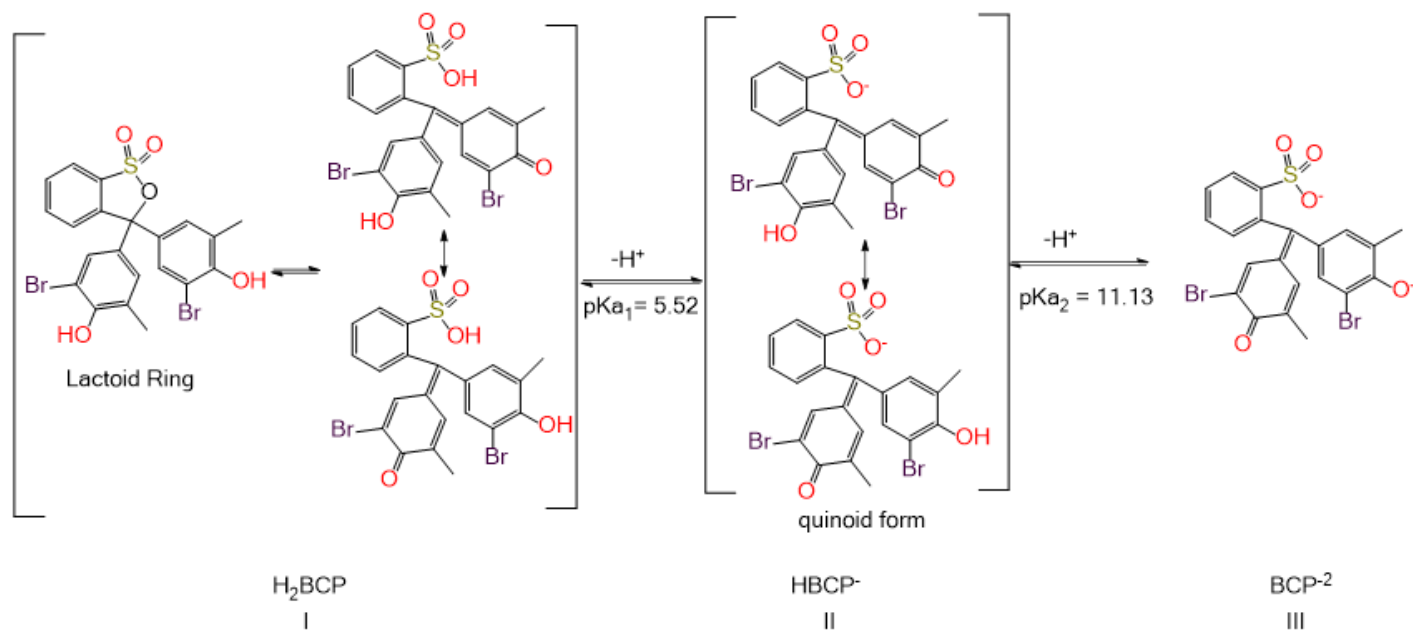


Figure 3

The possible dissociation mechanism of bromocresol purple.

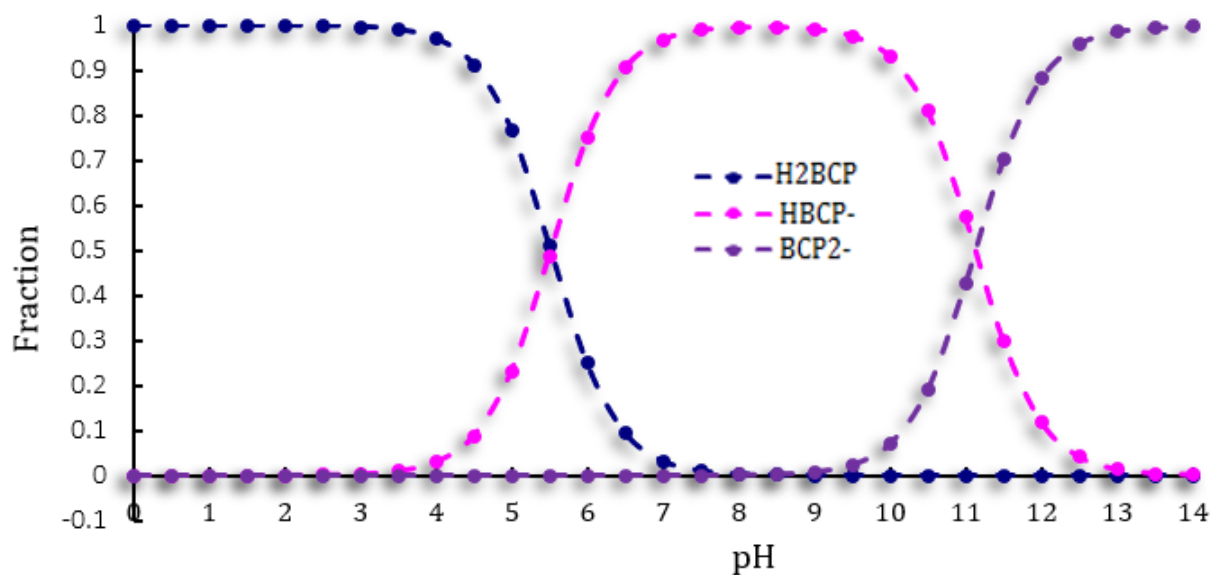


Figure 4

Distribution diagram of various species of bromocresol purple indicator in % 50 (v/v) water-ethanol at different pH's.

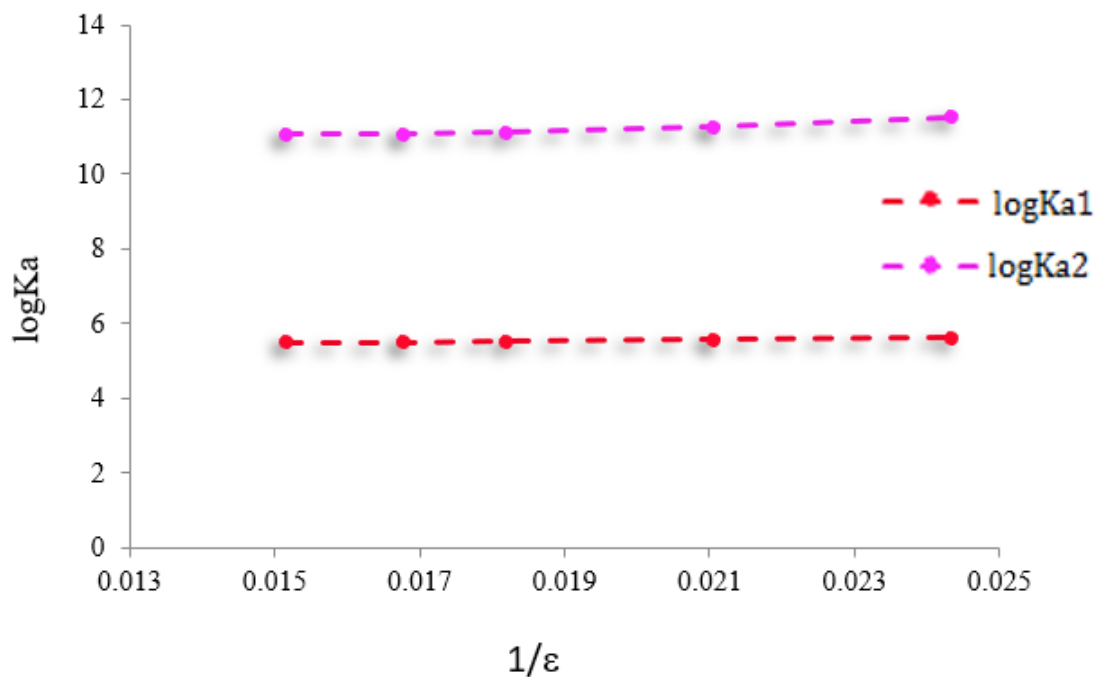


Figure 5

. The plot of pKa of 1.85×10^{-5} M solutions of bromocresol purple in aqueous ethanol blends with $1/\epsilon$ of the medium at room temperature.