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# Potentiometric Determination of the Dissociation Constant of Benzoic Acid in Aqueous Ethanol Solvents and Investigation of Effect of Solvent and Inorganic Salts on Spectroscopic Properties of Benzoic Acid Solutions by UV Absorbance Spectroscopy

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The dissociation constants of benzoic acid has been determined at 25 °C and an ionic strength of 5 mmol $L^{-1}$ in water and mixed aqueous solutions of ethanol (0.5–5%) by potentiometric measurements. A linear relationship between $pK_a$ and the mole fraction of the co-solvent was observed. In this study, the effect of concentration of ethanol in the solvent mixture and the adding inorganic salts to benzoic acid solutions on the absorbance of the solutions was examined. The measurements were performed by using a UV spectrophotometer. It has been shown that the solvents affect the dissociation equilibria and UV absorbance spectra of benzoic acid. This effect was related to the hydrogen bonding ability of the OH groups of the former class of anions.

**Key words: UV absorbance spectroscopy, Benzoic acid, Ionic effect, Water/ethanol mixed solvents, Dissociation constant.**

## INTRODUCTION

The effect of solvent composition on the dissociation equilibria of organic reagents is of great importance in chemical and biomedical analysis. For example, data of dissociation constant in mixed solvents can be used to plan many analytical procedures such as acid-base titration, extraction and complex formation in non-aqueous solutions. Therefore, studies on dissociation constants in non-aqueous and/or mixed solvents have attracted much attention in recent years[1].

In this work, the dissociation constants of benzoic acid have been determined potentiometrically at 25°C and ionic strength I = 5 mmol/L in water and in aqueous mixed solutions of ethanol (EtOH). The $pK_a$ values of the solutes can be changed by the ionic strength and, again, by varying the solvent composition. For our investigation, ethanol was selected, because this solvent is fully miscible with water, shows low absorbance in the common UV range, has considerably good solubility properties for ionic or ionizable analytes and is favorable for manipulation and toxic reasons[2]. The polarity of the solvent can be easily changed over a large range by changing the ratio of alcohol/water in the mixture and for this reason, these mixtures are useful in analytical techniques[3].

Molecular system interacts with molecular particles in the solutions. Therefore, thermodynamic and kinetic properties, chemical reactivity and electronic energy levels of the molecular systems are changed by this interaction. This interaction is determined by different physico-chemical methods. Particularly, change of electronic energy levels may be determined by UV absorbance spectroscopy. In this work, the solvent effect on the dissociation equilibria, the UV absorption spectra of benzoic acid are investigated. The interactions in the solutions change with amount of ethanol in ethanol-water solvent mixtures. Therefore, measured absorbance values of the solutions are also changed[4].

The position of most solution equilibria depends upon the electrolyte concentration of the medium. The concentration quotient for the equilibrium involves the dissociation of carboxylic acid as a function of electrolyte concentration. Extensive studies have revealed that the magnitude of the electrolyte effect is highly dependent upon the charges of the participants in an equilibrium. When only neutral species are involved, the position of equilibrium is essentially independent of electrolyte concentration. With ionic participants, the magnitude of the electrolyte effect increases with charge[5, 6].

In this work, the effect of species and concentration of the added inorganic salts on absorbance of the benzoic acid solutions was investigated. Both the ionic strength of the solution and the measured absorbance values of the solutions are changed by adding inorganic salts to media. The inorganic salts have different anionic and cationic valences.

## EXPERIMENTAL

The phosphate buffer and the organic solvents were purchased from Merck in AR grade. The inorganic salts obtained from Riedel-de Haen and E. Merck, Germany, Messrs. Fluka A.G and of purum grade were used as such.

A standard solution of $5.00 \times 10^{-5}$ M (1 M = 1 mol $dm^{-3}$) benzoic acid was prepared by dissolving 3.053 mg of the benzoic acid in an ethanol-water mixtures which have different mole ratio. The salts used in the present studies are NaCl, $Na_2SO_4$, $Na_3PO_4$, $CaCl_2$ and $FeCl_3$. The concentrations of every salt solution are $5.00 \times 10^{-5}$ M, $1.00 \times 10^{-4}$ M and $2.00 \times 10^{-4}$ M. Water was distilled and deionized with a MilliQ system (Milli-Q SP. TOC., Milipore).

The absorption spectra and absorbances were measured by a Varian 1E UV/Vis Spectrophotometer using a quartz cell with an optical path length of 1.0 cm. The temperature of the thermostatic bath was controlled within ±0.2°C in the range between 0° and 50°C.

The potentiometric determination of the apparent $pK_a$ values of the benzoic acid were carried out with a titration unit (model DL 67) equipped with a glass-calomel electrode (DG 101-SC); the same electrode was used for the preparation of the buffer electrolytes. It was filled with aqueous KCl, 3 mol $L^{-1}$, saturated with AgCl. Calibration was made with aqueous standard buffer solutions. Titrator was a solution of 100 mmol $L^{-1}$ NaOH.

### Potentiometric determination of the apparent $pK_a$

The apparent (non-thermodynamic) $pK_a$ values of the benzoic acid were determined by potentiometric titration. A Metter titration device equipped with a glass-calomel electrode filled with aqueous KCl, 3 mol/L, saturated with AgCl, was applied. The samples were titrated with 100 mmol/L NaOH. Presented $pK_a$ values were calculated in the usual manner by determining the pH at the half equivalent point. The final composition of the solvent at $pH = pK_a$ was determined by calculation.

### Procedure for determination of the ethanol effect on the absorbance spectra of the benzoic acid solutions

For the experiments, the solutions of benzoic acid were prepared by using ethanol-water mixtures. The concentration of the solutions is $5 \times 10^{-5}$ M. One of the solutions was prepared by using water only. Another solution was prepared by using different proportions of ethanol. The amount of the ethanol-water mixtures varies from 0.5 (v/v) to 5.0 (v/v) %. The experiments are made at 25°C.

Solvent mixtures were prepared from freshly opened bottles, using Brand II 25.00 mL burettes to transfer the liquids. The maximum wavelengths of the solutions were determined at 25°C.

The ethanol-water mixtures were used as solvents. The relationships between absorbances of the benzoic acid solutions and amount of ethanol in the solvent mixture were determined.

### Procedure for determination of the salt's effect on the absorbance spectra of the benzoic acid solutions

The solutions of benzoic acid of $5 \times 10^{-5}$ M were used in experiments. The solutions were prepared with ethanol-water mixture of 5.0%. The maximum wavelength of the solution was determined and this wavelength was used in measurements. Different inorganic salts were added to the solution as such, NaCl, $CaCl_2$, $FeCl_3$, $Na_2SO_4$ and $Na_3PO_3$. The concentrations of the added salts are $5 \times 10^{-5}$ M, $1 \times 10^{-4}$ M and $2 \times 10^{-4}$ M. The spectra were determined at 25°C . The relationships between absorbance of the benzoic acid solutions and species and concentration of the added salts were investigated.

## RESULTS AND DISCUSSION

### Effect of solvent on the dissociation equilibrium

The apparent $pK_a$ values of benzoic acid are given Table-1 for aqueous ethanolic solvents with up to about 5% (v/v) EtOH. The resulting increase of the $pK_a$ values upon addition of EtOH is shown in Fig. 1.

The value of $pK_a$ in water obtained in this work was 4.12, which is in excellent agreement with the values 4.12, 4.12, 4.19, 4.20 reported in literature[2, 5, 7–9]. In addition, the present $pK_a$ values in aqueous solutions, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 (v/v) % ethanol also agree well with those interpolated from the reported results[2, 9].

TABLE 1
OBSERVED $pK_a$ VALUES OF BENZOIC ACID IN WATER AND IN MIXED AQUEOUS-ETHANOLIC SOLUTIONS

| % (v/v) EtOH | Observed $pK_a$ values of benzoic acid |
|---|---|
| 0.0 | 4.1205 |
| 0.5 | 4.1238 |
| 1.0 | 4.1309 |
| 1.5 | 4.1384 |
| 2.0 | 4.1461 |
| 2.5 | 4.1539 |
| 5.0 | 4.1970 |

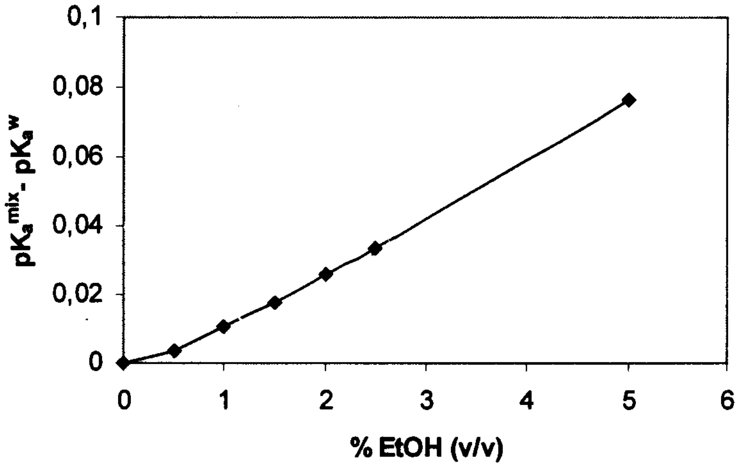

Fig. 1. Effect of the composition of the mixed aqueous-ethanolic solvent (mix) on the observed, mixed-mode $pK_a$ values of benzoic acid, compared to water (w). The $pK_a$ values were determined by potentiometric titration. Ionic strength, I = 5 mmol/L.

The variation of $pK_a$ as a function of mole fraction ($X_2$) of the co-solvent in the mixed solvents is shown in Fig. 1. As can be seen, there is a linear relation between $pK_a$ and $X_2$ in a limited range of co-solvent compositions. The slope may be considered as a measure of co-solvent effect on $pK_a$ in the water-rich media.

The result of the $pK_a$ dependence on the ethanol concentration can be interpreted by several concepts. One is based on electrostatic interactions; according to Born's theory, another concept considers aqueous-ethanolic mixtures as a ternary solvent, consisting of cluster of water, ethanol and combined water ethanol species[9, 10]; the longest established concept is that of the medium effect, ln $\gamma_i^m$ (or log $\gamma_i^m$), given by

$$\ln \gamma_i^m = \frac{(\omega_1^0)_{mix} - (\omega_i^0)_{water}}{RT} \quad (1)$$

Here the transfer activity coefficient or medium activity coefficient, $\gamma_i^m$, is defined as $\gamma_i^m - \gamma_{i,\,mix} / \gamma_{i,\,water}$; $\gamma_{i,\,mix}$ and $\gamma_{i,\,water}$ are the activity coefficients of species *i* in the mixed solvent and water respectively. $\omega_i^0$ is the chemical potential of component *i* in the standard state, R is the gas constant and T the absolute temperature.

According to this model[8, 10, 11], the reversible work for the transfer of 1 mole of species i from infinite dilution in water to infinite dilution in solvent S is related to the medium effect. If the mixed solvent better stabilizes the particles of species i than water, the medium effect has a negative value and *vice versa*. When applied to the proton, the medium effect is a measure for the basicity of the solvent S relative to water.

For the case under consideration, the neutral acid HA undergoes the dissociation equilibrium $HA = H^+ + A^-$ in both solvents. The destabilization of the anion seems to exert a major influence on the $pK_a$ value since ethanol has a worse solvating ability towards anions compared to water. Consequently log $\gamma_{A^-}^m$ has positive and large values showing that the medium effect on the anion dominates, resulting in an increase of $pK_a$ values when ethanol is added to water[8, 12, 13].

The above discussion is directed to the solvation of the anion, mainly concerning the negatively charged group in the molecule. A possible lipophilic interaction of the methyl group of the alcohol with the aromatic ring or the lipophilic substituent is not taken into account in the same way as a possible hydrogen bonding of the OH groups of the solute with that of the solvent.

## Effect of ethanol on the absorbance spectra of the benzoic acid solutions

The effect of amount of ethanol [0.5 (v/v)–5 (v/v) %] in the solvent mixture on the absorbance of the solutions was examined. The results are shown in Fig. 2. The absorbances at the absorption maximum increased along with an increase in amount of ethanol in the solvent mixture (Fig. 2), because the structure of the investigated molecule changes due to the solute-solvent and solvent-solvent interaction.

Electronic transition possibility is changed with amount of ethanol in the solvent mixture[14]. The mole ratio of the solvent mixture affects the absorbance. Additionally, structure of the H-bonding is changed with the mole ratio of the solvent mixture. The influence of amount of solvents in the mixture on the structure and other physico-chemical properties is shown in Fig. 2.

Altered solvatochromism might have arisen from specific interactions between the solvent molecules. Such interactions can lead to the information of new species (*via* hydrogen bonding between ethanol and water)[15].

The results show that the mixture components interact with one another and that the interactions affect the absorbance of the solutions[3] . The absorbance of the solutions behaves as expected. It increases slightly with increasing amount of ethanol in the solvent mixtures. The result is shown in Fig. 2.

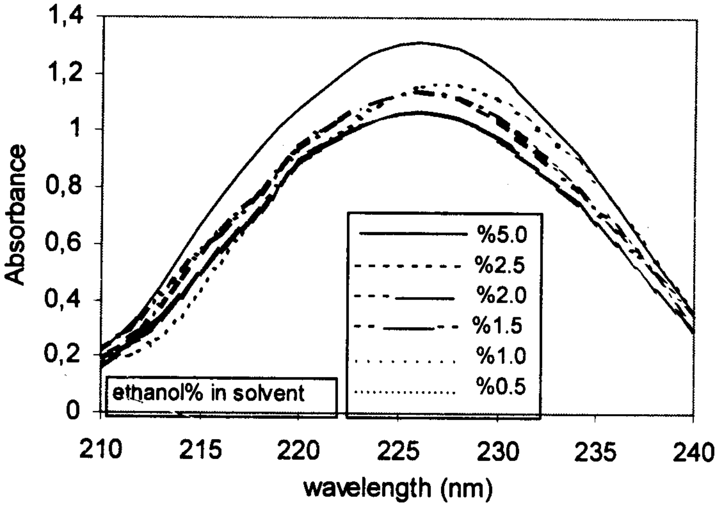

Fig. 2. Absorbance spectra of the benzoic acid solutions in ethanol-water solvent mixture. The mole ratio of ethanol in the solvent mixture are 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0%. Operating conditions: blank solution ethanol-water mixture; quartz vessel with 1 mm optical path length; signal acquisition in 0.5 nm steps; mean acquisition time 1 s per data point; double-beam mode with air reference; 2 nm bandwidth; temperature: 25°C.

## Effect of the inorganic salts on the absorbance spectra of the benzoic acid solutions

Systematic studies have shown that the effect of added electrolyte on equilibria is independent of chemical nature of the electrolyte but depends upon a property of the solution called the ionic strength. The ionic strength of a solution of a strong electrolyte consisting solely of singly charged ions is identical with its total molar salt concentration. The ionic strength is greater than the molar concentration if the solution contains ions with multiple charges[4].

For solutions with ionic strengths of 0.1 M or less, the electrolyte effect is independent of the kind of ions and dependent only upon the ionic strength. This independence with respect to electrolyte species disappears at high ionic strengths[4]. In the present study, the effect of species of the inorganic salts on the absorbance of the benzoic acid solutions was examined. The results are shown in Fig. 8. According to the results, species of the inorganic salts affect the change of absorbance of the solutions.

The effect of the added salt with varying concentrations ($5 \times 10^{-5}$ M, $1 \times 10^{-4}$ M and $2 \times 10^{-4}$ M) on the absorbance of the benzoic acid solutions was examined. The results are shown in Figs. 3–7. The addition of inorganic salts affected the shift of the wavelength. As shown in Figs. 3–7, the absorbance values of the solutions decrease along with an increase in the inorganic salt concentrations. In this study, the effect of adding inorganic salts to the solutions on the transition possibility of the molecule was examined. Ionization of the compounds increases with increase in the ionic strength. Interaction between ions in the solutions decreases with increase in the ionic strength. Therefore association of

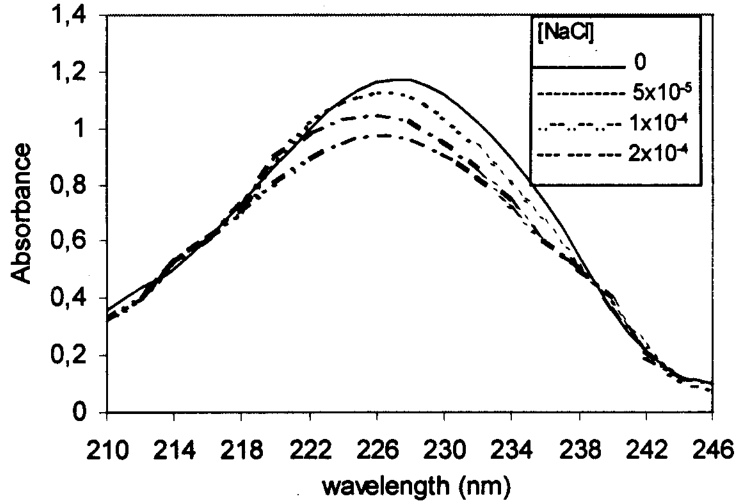

Fig. 3. Influence of ionic strength of the medium (NaCl at various concentrations) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M; the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

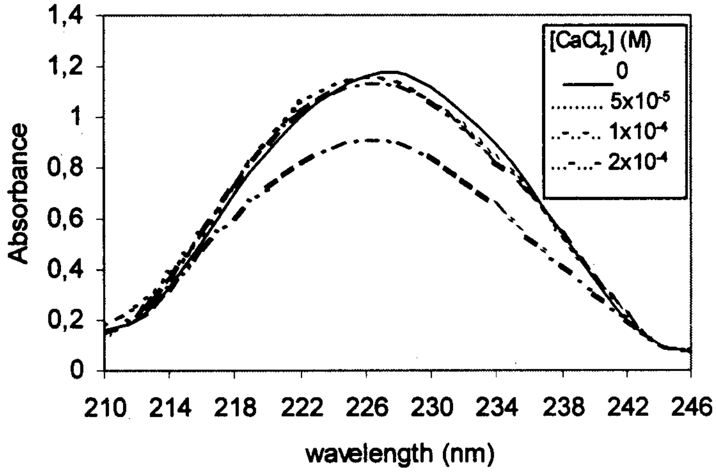

Fig. 4. Influence of ionic strength of the medium ($CaCl_2$ at various concentrations) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M; the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

the ions in the solutions decreases with this effect but solvation in the solutions increases. The electrostatic potential of medium has different values due to change of charge valance of the ions of the salts. Thus, stability and electronic transition possibility of the molecular structure changes by forming activity[16].

The absorbance decreases and stability of the molecular structure increases

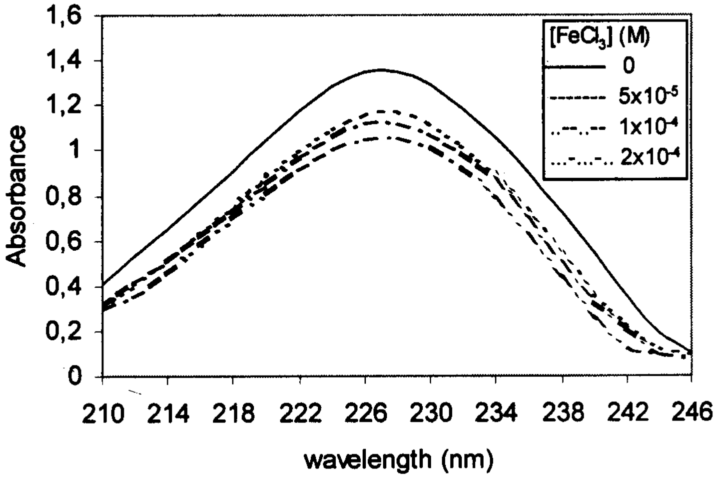

Fig. 5. Influence of ionic strength of the medium ($FeCl_3$ at various concentrations) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M; the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

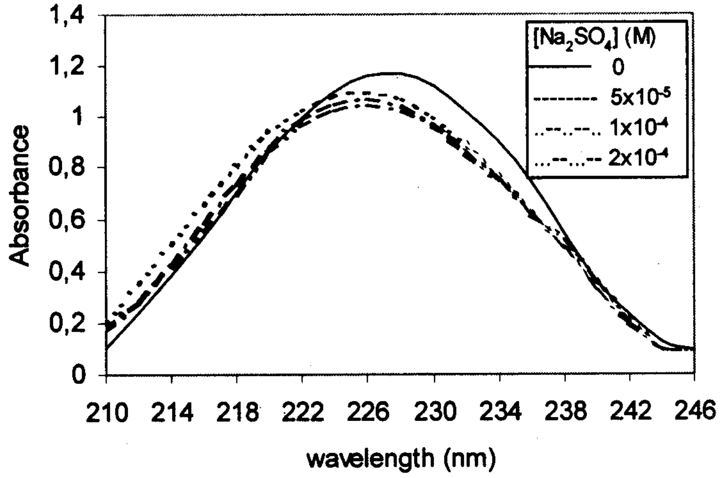

Fig. 6. Influence of ionic strength of the medium ($Na_2SO_4$ at various concentrations) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M ; the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

with addition of the salts and thus, electronic transition possibility of the molecules decreased with change of ionic strength (Figs. 3–7). Electronic transition possibility of the molecule is affected by the presence of electrolyte in the solution.

Added $Na_3PO_4$ to the solution affects the shift of the wavelength (Fig. 7). The

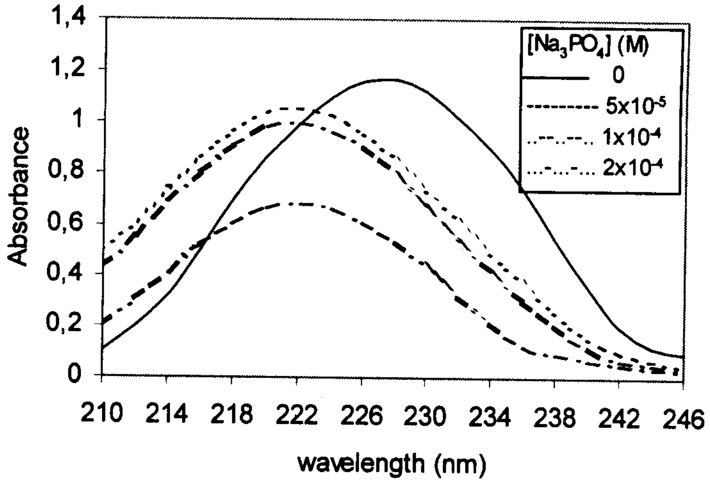

Fig. 7. Influence of ionic strength of the medium ($Na_3PO_4$ at various concentrations) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

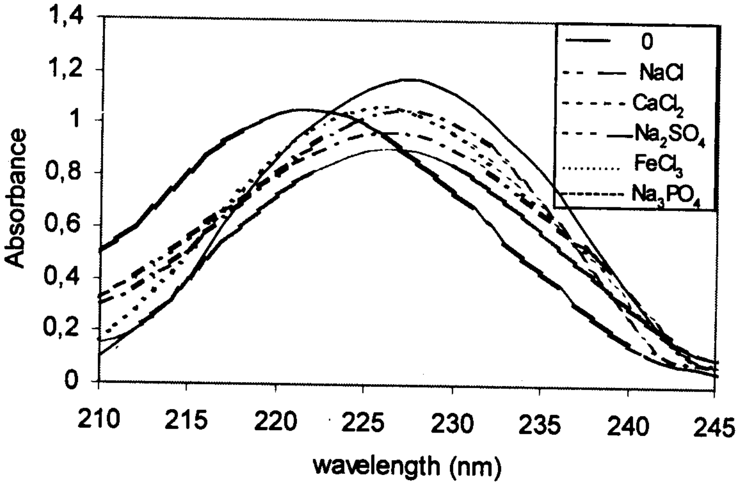

Fig. 8. Influence of species of the salts (the concentration of the salts is $5.0 \times 10^{-5}$ M) on the shape of the benzoic acid solutions UV absorbance spectrum. The concentration of benzoic acid solutions: $5.0 \times 10^{-5}$ M; the mole ratio of ethanol in the solvent mixture is 5.0%; other conditions are as in Fig. 1.

absorption maximum of the benzoic acid solutions will shift to lower energies as the polarity and acidity of the medium increase. The dissociation of the benzoic acid increases with adding $Na_3PO_4$ to the solution. Molecular structure are changed by this effect and thus the wavelength of the molecule is also changed[17]

The electrolyte effect results from the electrostatic attractive and repulsive forces that exist between the ions of an electrolyte and the ions involved in an equilibrium. These forces cause each ion from the dissociated reactant to be surrounded by a sheath of solution that contains a slight excess of electrolyte ions of opposite charge. Debye and Hückel[18] derived a theoretical expression that permits the calculation of activity coefficients of ions from their charge and average size as

$$-\log f_x = \frac{0.51 Z_x^2 \sqrt{\mu}}{1 + 0.33 \alpha_x \sqrt{\mu}} \qquad (2)$$

where $f_x$ = activity coefficient of the species X
$Z_x$ = charge on the species X
$\mu$ = ionic strength of the solution
$\alpha_x$ = effective diameter of the hydrated ion X (Å)

Experimental determination of single-ion activity coefficients is unfortunately impossible because all experimental methods give only a mean activity coefficient for the positively and negatively charged ions in a solution. In other words, it is impossible to measure the properties of individual ions in the presence of counter ions of opposite charge and solvent molecules[4]. The mean activity coefficient of the electrolyte $A_mB_n$ is defined as,

$$f_\pm = \text{mean activity coefficient} = (f_A^m \cdot f_B^n)^{1/(m+n)} \qquad (3)$$

As the ionic strength increases an ion loses some of its effectiveness and its activity coefficient decreases (Table-2). In solutions that are not too concentrated, the activity coefficient for a given species is independent of the nature of the electrolyte and depends only upon the ionic strength. For a given ionic strength, the activity coefficient of an ion departs farther from unity as the charge carried by the species increases.

TABLE-2
IONIC STRENGTHS AND MEAN ACTIVITY COEFFICIENTS OF ELECTROLYTES

| Electrolytes | Ionic strength | Mean activity coefficient |
|---|---|---|
| NaCl | $5 \times 10^{-5}$ | 0.994 |
| | $1 \times 10^{-4}$ | 0.998 |
| | $2 \times 10^{-4}$ | 0.983 |
| $CaCl_2$ | $1.5 \times 10^{-4}$ | 0.775 |
| | $3.0 \times 10^{-4}$ | 0.699 |
| | $6.0 \times 10^{-4}$ | 0.607 |
| $FeCl_3$ | $3.0 \times 10^{-4}$ | 0.391 |
| | $6.0 \times 10^{-4}$ | 0.271 |
| | $1.2 \times 10^{-3}$ | 0.164 |
| $Na_2SO_4$ | $1.5 \times 10^{-4}$ | 0.760 |
| | $3.0 \times 10^{-4}$ | 0.699 |
| | $6.0 \times 10^{-4}$ | 0.605 |
| $Na_3PO_4$ | $3.0 \times 10^{-4}$ | 0.383 |
| | $6.0 \times 10^{-4}$ | 0.260 |
| | $1.2 \times 10^{-4}$ | 0.155 |

## Conclusions

Dissociation equilibrium is sensitive to the polarity of the solvent. On the other hand, the transition energy of the benzoic acid is also changed because of shift of the dissociation equilibrium in the mixed solvents. In this work, the effect of the solvent on the dissociation equilibrium and absorbance spectra of the benzoic acid were determined by potentiometric and UV absorbance spectroscopy methods. The results of these methods are agree with each other.

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