

## Spectrophotometric study of acid-base equilibria of 4-(2-benzothiazolylo-azo)resorcinol and 4-(2-benzothiazolylo-azo)salicylic acid

Mohamed S Abu-Bakr\*, Anwar S El-Shahawy & Seddique M Ahmed  
Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

Received 16 November 1992; revised and accepted 7 April 1993

The visible absorption spectra of 4-(2-benzothiazolylo-azo)resorcinol and 4-(2-benzothiazolylo-azo)salicylic acid have been recorded in aquo-organic solvent mixtures in the pH range 0.5-12.0. The spectral changes have been explained in terms of shifts in equilibria amongst different molecular and ionic species of BTAR and BTAS existing in solution. The  $pK_a$  values corresponding to the different ionisation steps have been determined at 25°C and  $I=0.1 M$  ( $KNO_3$ ) by graphical analysis of the absorbance-pH curves.

Though thiazolylo and benzothiazolylo phenol derivatives form an interesting class of reagents for spectrophotometric determination of several metal ions<sup>1-6</sup>, no solution studies have so far been reported on the acid-base equilibria of the two benzothiazolylo azophenol derivatives, viz., 4-(2-benzothiazolylo-azo)resorcinol (BTAR) and 4-(2-benzothiazolylo-azo)salicylic acid (BTAS).

In the present work, a spectrophotometric study of the acid-base equilibria of BTAR and BTAS in water-organic solvent mixtures of varying pH's containing 20, 40 and 60% (v/v) of the solvent at  $I=0.1 M$  ( $KNO_3$ ), has been reported. The solvents used are methanol, ethanol, *n*-propanol, iso-propanol, acetone, dioxane and dimethyl formamide. The acid dissociation constants of the two reagents have also been determined from the graphical analysis of the spectral data.

### Materials and Methods

The two reagents BTAR and BTAS were synthesized and recrystallized by the reported method<sup>7</sup>. The purity of the compounds was checked by elemental analysis, melting point and TLC<sup>8</sup>. Stock solutions of BTAR ( $3.0 \times 10^{-4} M$ ) and BTAS ( $5.0 \times 10^{-4} M$ ) were prepared in the required solvent. The organic solvents, methanol, ethanol, *n*-propanol, iso-propanol, acetone, dioxane or DMF used were either of spectroscopic pure grade (Spectrosol) from BDH or were purified by conventional methods<sup>9</sup>. All the other chemicals used were of AR grade. Doubly distilled water was used in the experiments. The pH of the solutions was maintained with nitric acid or KOH

and the ionic strength was maintained at  $I=0.1 M$  ( $KNO_3$ ).

The absorption spectra were recorded on a Shimadzu UV 200 S double-beam spectrophotometer at 25°C using 1 cm matched stoppered quartz cells. The spectrophotometric measurements were made within the wavelength range 320-650 nm. The pH-measurements were made using a Radiometer Model M 63 pH meter equipped with a glass-calomel combination electrode. The pH values in partially aqueous solutions were corrected as described by Douheret<sup>10</sup>.

### Results and Discussion

Depending on the acidity of the medium, the solution of BTAR contains four different acid-base forms, viz.,  $LH_3^+$ ,  $LH_2$ ,  $LH^-$  and  $L^{2-}$ . The monoprotonated species,  $LH_3^+$ , (460 nm) is present in strong acid medium ( $pH < 1.0$ ). In the pH range ~ 1.0-3.5 the solution contains the yellow neutral form (440 nm). The spectrum of BTAR in media of pH 4.0-6.0 exhibits an absorption band at 470 nm. This behaviour indicates the presence of the monoanionic form of BTAR. At relatively higher pH values of 7.0-10.5, the spectrum exhibits a new absorption band at 520 nm denoting the doubly ionized form of BTAR.

These spectral changes are assumed to accompany the transformation of the neutral form  $LH_2$  to the monoanionic species  $LH^-$ . The orange  $LH^-$  species existing in the pH range 4.0-6.0 is converted into the red dianionic  $L^{2-}$  at pH 6.5-10.5, above which the spectrum exhibits no band shift or intensity changes.

The acid-base equilibria of BTAR have been

studied in media containing 20, 40 and 60% (v/v) of the organic co-solvent in the pH range ~0.5-12.0. The organic solvents used are methanol, ethanol, *n*-propanol, iso-propanol, acetone, dioxane and DMF. The absorption spectra of  $3.0 \times 10^{-5} M$  solution of the reagent at various concentrations of HNO<sub>3</sub> or KOH were recorded as the dependence  $A = F(\lambda)$  for various pH values. The spectra of this reagent in all mixtures investigated display three main absorption bands within the pH range 1.0-12.0. The maximum absorption of these bands is located at (430-455 nm), (440-470 nm) and (508-525 nm) respectively. These bands presumably denote absorption due to the neutral molecules, monoionized, and doubly negatively charged species. The absorbance of each of these bands depends upon the pH of the solution as well as its composition. All bands undergo a regular shift to longer wavelengths on increasing pH. In solutions of the same pH and constant proportion of the organic co-solvent, the values of  $\epsilon_{\max}$  for the bands at longer wavelengths decrease in the order DMF > dioxane > acetone > iso-propanol > *n*-propanol > ethanol > methanol.

The increase of pH, however leads to the development of an absorption band near 440-470 nm which probably corresponds to the formation of a mononegatively charged species. The absorbance of this band is lower than that due to neutral molecules and decreases gradually with rise in pH of the medium. Above pH 6.0, the band exhibits a red shift and its absorbance increases gradually.

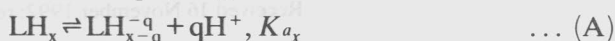
The absorption curves of BTAR within the pH range 6.0-8.0 intercept near the wavelength ~450-470 nm. The resulting isobestic point may be due to the equilibrium existing in solution between the mono and divalent anions of BTAR.

In aqueous-alcohol or acetone media, the transformation of univalent to divalent anions takes place at pH > 7, but it starts to occur at relatively lower pH 6.0-6.5 in aqueous-solvent mixtures containing high proportions of DMF or dioxane. The band due to the absorbance by the neutral molecules, which is located near 440 nm attains at pH 1.0-3.0, a maximum value which depends primarily on the nature of the solvent used. The value of the molar absorptivity  $\epsilon_{\max}$  for this band is also affected by the percentage of organic solvents.

The absorbance values of BTAR at two different specific wavelengths were examined as a function of pH for the different solutions of BTAR investigated. The variation of absorbance with pH illustrates the effect of both the nature and the composition of the medium (Fig. 1). The dissociation

constants of BTAR in various media were evaluated from the individual formation regions of the absorbance-pH curves by graphical analysis<sup>11-14</sup>.

The transformations are derived from the equations for the equilibrium constant and mass balance equations, combined with the equation for total absorbance of the solution (assuming the validity of Beers law). After simple rearrangement one obtains<sup>14</sup> for the equilibrium (A), the transformations Eqs. (1-4),



$$A = \epsilon_1 C_L + K_{a_x} (\epsilon_2 C_L - A) / [\text{H}^+]^q = A_{01} + F_1 K_{a_x} \dots (1)$$

$$A = \epsilon_2 C_L - (A - \epsilon_1 C_L) K_{a_x}^{-1} [\text{H}^+]^q = A_{02} - F_2 K_{a_x}^{-1} \dots (2)$$

$$C_L/A = 1/\epsilon_1 - (C_L \epsilon_2 - A) [\text{H}^+]^{-q} A^{-1} \epsilon_1^{-1} K_{a_x} \\ = \epsilon_1^{-1} - Q_1 [\text{H}^+]^{-q} \quad \dots (3)$$

$$C_L/A = 1/\epsilon_2 + (A - C_L \epsilon_1) [\text{H}^+]^q A^{-1} \epsilon_2^{-1} K_{a_x}^{-1} \\ = \epsilon_2^{-1} + Q_2 [\text{H}^+]^q \quad \dots (4)$$

where A is the absorbance, C<sub>L</sub> is the total reagent concentration,  $\epsilon_1$  and  $\epsilon_2$  are molar absorption coefficients,  $K_{a_x}$  is the equilibrium constant of the reaction (A), and the other symbols are self ex-

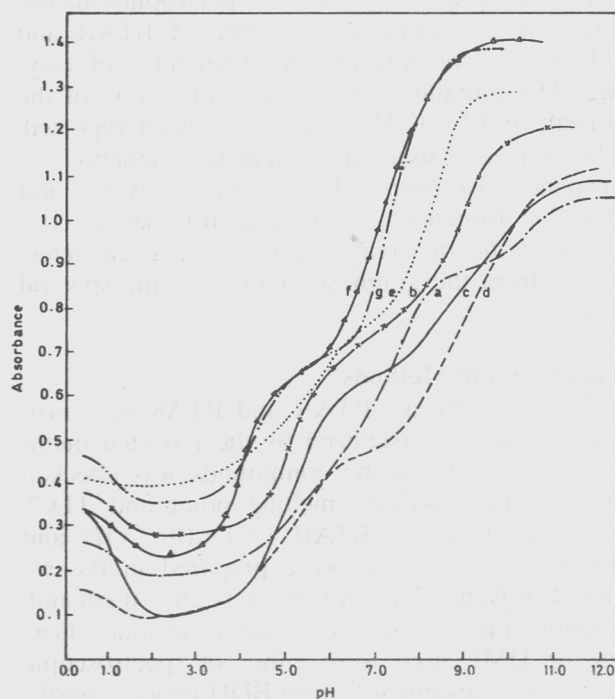


Fig. 1—Variation of absorbance with pH for solutions of  $3.0 \times 10^{-5} M$  (BTAR) in different water-organic solvent mixtures, 40% (v/v) organic solvent: a) methanol; b) ethanol; c) *n*-propanol; d) iso-propanol; e) acetone; f) dioxane; and g) DMF; at  $\lambda = 520 \text{ nm}$ .

planatory. The plots of  $A=f(F_1 \text{ or } F_2)$  and  $C_L/A=f(Q[H^+]^{-q} \text{ or } Q_2[H^+]^q)$  were linear. The values of the dissociation constants were obtained from the slopes of these linear plots. More precise values of  $K$  could be evaluated using the "graphical logarithmic analysis". The corresponding Eq. (5) can be derived from any one of the Eqs. (1-4).

$$\log \frac{A - \epsilon_1 C_L}{\epsilon_2 C_L - A} = q \text{ pH} - pK_{a_x} \quad \dots (5)$$

The slope of the plot  $\log [(A - A_{01})/(A_{02} - A)]$  versus  $f(\text{pH})$  gives the number of protons ( $q$ ) liberated in the acid-base equilibrium ( $q=1$  for reaction A). The value of  $\text{pH}$  at which  $\log [(A - A_{01})/(A_{02} - A)]$  is equal to zero determines the value of  $\text{pH}_{a_x}/q$ .

The procedure described above was applied separately to each wavelength and from the series of  $pK_{a_x}$  values, mean values were calculated. The deviation from the mean  $pK$  values were evaluated using Eq. (6),

$$\sigma(p\bar{K}) = \left[ \frac{1}{N_\lambda} \sum_{n=1}^{N_\lambda} (p\bar{K} - pK_n)^2 \right] \quad \dots (6)$$

where  $p\bar{K}$  is the mean value calculated from  $pK$

values obtained from curves for individual wavelength  $n$  and  $N_\lambda$  is the number of wavelengths used. The values of the dissociation constants were also calculated using the general least squares program LETAGROP-SPEFO of Sillen and Warnqvist<sup>15</sup> by treating the original data [ $A=f(\text{pH})$ ] and minimizing the residual squares sum function  $U$ . The  $pK_a$  values corresponding to the different ionization steps of BTAR are shown in Table 1. The values obtained by analysis of the absorbance versus  $\text{pH}$  graphs using Eq. (5) are in good agreement with those calculated by the regression method. The distribution curves for the different species of BTAR (40% v/v methanol) computed from the acid dissociation constants of the reagent are shown in Fig. 2.

The absorption spectra of BTAS show four absorption bands within the  $\text{pH}$  range  $\sim \leq 1.0-11.5$  in all aqueous organic solvent mixtures investigated. The band appearing at 460 nm in strongly acidic solutions ( $\text{pH} \leq 0.8$ ) is presumably due to absorption by the cationic form ( $\text{LH}_3^+$ ) of the reagent. The absorption band at  $\lambda=405-415$  nm in the  $\text{pH}$  1.0-3.0, is presumably due to the neutral species ( $\text{LH}_2$ ). At  $\text{pH}$  3.0-5.0 the spectrum of BTAS exhibits an absorption band with  $\lambda_{\text{max}}$  at 420-435

Table 1—Mean  $pK_{a_i}$  value\* of 4-(2-benzothiazolylazo)resorcinol (BTAR) and 4-(2-benzothiazolylazo)salicylic acid (BTAS) in different water-organic solvent mixtures [Temp. = 25°C; I = 0.1M(KNO<sub>3</sub>)]

Organic solvent	% (v/v)	BTAR				BTAS			
		$pK_{a1} (\text{LH}_2/\text{LH}^-)$		$pK_{a2} (\text{LH}^-/\text{L}^{2-})$		$pK_{a1} (\text{LH}_2/\text{LH}^-)$		$pK_{a2} (\text{LH}^-/\text{L}^{2-})$	
		Graphical analysis	Regression procedure	Graphical analysis	Regression procedure	Graphical analysis	Regression procedure	Graphical analysis	Regression procedure
Methanol	20	6.20 ± 0.03	6.25 ± 0.010	10.30 ± 0.01	10.28 ± 0.01	3.08 ± 0.02	3.10 ± 0.01	10.15 ± 0.01	10.14 ± 0.03
	40	6.55 ± 0.02	6.58 ± 0.008	10.35 ± 0.03	10.33 ± 0.01	4.05 ± 0.01	4.03 ± 0.02	10.50 ± 0.03	10.53 ± 0.02
	60	6.65 ± 0.04	6.67 ± 0.013	10.40 ± 0.02	10.37 ± 0.03	5.65 ± 0.03	5.67 ± 0.01	10.70 ± 0.02	10.72 ± 0.02
Ethanol	20	5.10 ± 0.05	5.15 ± 0.04	8.60 ± 0.04	8.62 ± 0.03	3.20 ± 0.02	3.18 ± 0.01	8.90 ± 0.02	8.93 ± 0.01
	40	5.17 ± 0.01	5.13 ± 0.02	8.75 ± 0.05	8.73 ± 0.01	3.40 ± 0.01	3.43 ± 0.01	9.22 ± 0.03	9.17 ± 0.04
	60	5.32 ± 0.03	5.34 ± 0.01	9.15 ± 0.02	9.12 ± 0.02	3.65 ± 0.04	3.68 ± 0.02	9.63 ± 0.04	9.61 ± 0.01
<i>n</i> -Propanol	20	4.55 ± 0.02	4.57 ± 0.03	8.27 ± 0.04	8.25 ± 0.01	3.30 ± 0.03	3.32 ± 0.02	9.75 ± 0.03	9.78 ± 0.02
	40	4.95 ± 0.03	4.92 ± 0.02	9.05 ± 0.02	9.07 ± 0.02	3.45 ± 0.02	3.40 ± 0.03	10.00 ± 0.03	10.02 ± 0.02
	60	5.10 ± 0.01	5.12 ± 0.01	9.20 ± 0.01	9.23 ± 0.01	3.55 ± 0.02	3.52 ± 0.01	10.10 ± 0.02	10.13 ± 0.01
<i>iso</i> -Propanol	20	4.75 ± 0.04	4.76 ± 0.04	8.70 ± 0.03	8.72 ± 0.03	4.50 ± 0.03	4.52 ± 0.01	9.80 ± 0.02	9.82 ± 0.01
	40	5.00 ± 0.02	4.97 ± 0.03	9.10 ± 0.02	9.13 ± 0.01	4.60 ± 0.04	4.63 ± 0.01	10.05 ± 0.03	10.03 ± 0.03
	60	5.22 ± 0.01	5.24 ± 0.01	9.40 ± 0.04	9.44 ± 0.02	4.70 ± 0.05	4.72 ± 0.02	10.15 ± 0.04	10.16 ± 0.02
Acetone	20	5.51 ± 0.05	5.48 ± 0.05	8.15 ± 0.02	8.13 ± 0.02	5.62 ± 0.03	5.64 ± 0.02	9.60 ± 0.03	9.63 ± 0.01
	40	5.30 ± 0.03	5.25 ± 0.03	8.30 ± 0.03	8.13 ± 0.02	5.70 ± 0.04	5.68 ± 0.05	10.15 ± 0.02	10.11 ± 0.03
	60	5.75 ± 0.02	5.77 ± 0.01	8.50 ± 0.04	8.53 ± 0.02	6.00 ± 0.02	6.02 ± 0.03	10.31 ± 0.03	10.26 ± 0.05
Dioxane	20	4.52 ± 0.03	4.54 ± 0.02	7.50 ± 0.01	7.53 ± 0.01	3.40 ± 0.02	3.43 ± 0.02	8.40 ± 0.04	8.41 ± 0.02
	40	4.15 ± 0.01	4.18 ± 0.02	7.40 ± 0.03	7.38 ± 0.03	3.20 ± 0.03	3.21 ± 0.03	8.70 ± 0.02	8.67 ± 0.03
	60	4.05 ± 0.04	4.04 ± 0.01	7.25 ± 0.02	7.28 ± 0.02	3.12 ± 0.04	3.16 ± 0.01	8.95 ± 0.03	8.90 ± 0.03
DMF	20	4.55 ± 0.03	4.56 ± 0.03	7.60 ± 0.01	7.62 ± 0.02	3.15 ± 0.04	3.17 ± 0.02	8.65 ± 0.02	8.67 ± 0.01
	40	4.38 ± 0.01	4.36 ± 0.02	7.50 ± 0.03	7.48 ± 0.01	2.95 ± 0.03	2.92 ± 0.01	8.55 ± 0.01	8.52 ± 0.03
	60	4.25 ± 0.04	4.27 ± 0.01	7.25 ± 0.02	7.28 ± 0.01	2.80 ± 0.05	2.85 ± 0.03	8.10 ± 0.03	8.05 ± 0.04

\*Values resulting as a mean from the values calculated for each wavelength.

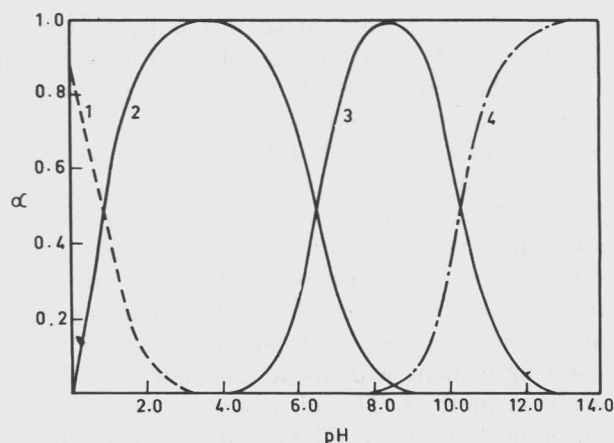
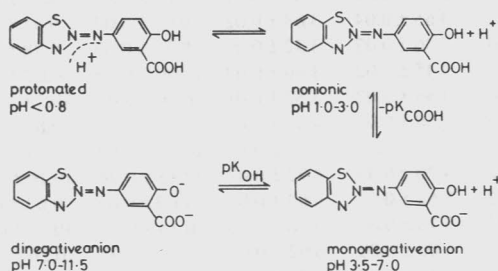


Fig. 2—Distribution curves for different acid-base forms of BTAR [40% (v/v) methanol,  $I=0.1 M$   $KNO_3$ ,  $25^\circ C$ ;  $C_L=3.0 \times 10^{-5} M$ ;  $\alpha=(1) [LH_3^+]/C_L$ ; (2)  $[LH_2]/C_L$ , (3)  $[LH^-]/C_L$  and (4)  $[L^{2-}]/C_L$ .

nm. The latter band corresponds to absorption by the monoanionic form of BTAS and suffers a red shift on decreasing acidity of the medium. The spectrum of BTAS displays a symmetrical and intense band with  $\lambda_{max}$  at 515-535 nm in the pH range 7.5-11.5, corresponding to the dianionic form ( $L^{2-}$ ) of the reagent. The absorption versus pH-graphs obtained at 420 nm show the various acid-base equilibria which exist in solution (Fig. 3).

It was concluded that the cationic species is the predominant form of BTAS in solutions of  $pH < 0.8$ . The neutral molecules of BTAS ( $LH_2$ ) exist as the prevalent species at pH values of 1.0-3.0. The transformation of the latter form to the monoanionic species ( $LH^-$ ) occurs at pH 3.5-7.0, above which elimination of another proton leading to the formation of the bivalent anion ( $L^{2-}$ ) is assumed. The different acid-base equilibria that may occur in solutions of BTAS can be represented by the following scheme,



The  $pK_a$  values and the corresponding acid base equilibria are given in Table 1.

The  $pK_a$  values corresponding to the different ionisation steps of BTAR and BTAS, are influenced by both the nature and amount of organic solvent used. The elimination of the proton from

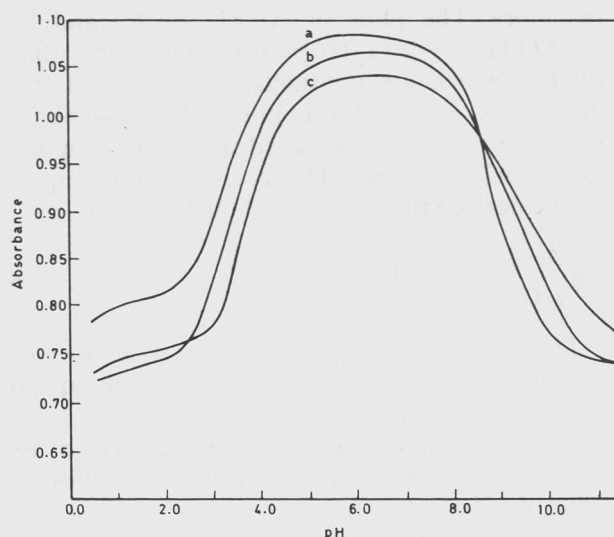


Fig. 3—Plot of absorbance versus pH of  $5 \times 10^{-5} M$  (BTAS) in different percentages of aqueous-organic solvent mixtures at  $\lambda=420$  nm. (a) 20% (v/v) ethanol; (b) 40% (v/v) ethanol; (c) 60% (v/v) ethanol.

COOH or OH is enhanced as the amount of DMF is increased but diminishes as the proportion of methanol, ethanol, acetone or dioxane is increased in solution. This behaviour can be explained by the fact that the former solvent acts as a proton acceptor rather than donor and causes protonation of the lone pairs of electrons on the COOH and OH groups facilitating proton dissociation. The decrease of ionisation on increasing the alcohol or acetone content in solution may be attributed to the blocking of the  $\pi$  electrons of the C=O groups by solvent molecules. The bands undergo a bathochromic shift on increasing the concentration of DMF in solution. This behaviour depends on solvation effect rather than on the dielectric properties. The band shift to shorter wavelength caused by increasing the proportion of dioxane can be attributed to the decrease of the concentration of the ionised forms as a result of ionic association.

The  $pK_a$  values obtained in solutions containing the same percentage of different organic solvents follow the order, DMF < dioxane < acetone < *n*-propanol < ethanol < isopropanol < methanol. This is presumably due to a decrease in the tendency of the solvent to associate with the solute through H-bond. Acetone is characterized by a very weak tendency to donate hydrogen bond<sup>16</sup>. The lowest  $pK_a$  value in DMF is because of its high basic character facilitating the ionisation process.

During the course of this study we observed that the two  $pK_a$  values for BTAR (Table 1) are due to the deprotonation of the *p* and *o*-OH

group mainly from the resorcinol part. In BTAS,  $pK_{a1}$  is due to the ionisation of a proton from the carboxylic group, whereas  $pK_{a2}$  is assigned to the ionisation of the phenolic-OH group. Also, on comparing the  $pK_a$  values of BTAR and BTAS (in 20% v/v ethanol) with their analogues, 2-(thiazolylazo)resorcinol (TAR) and 2-(thiazolylazo)salicylic acid (TAS), it is obvious that the  $pK_a$  values of BTAR (5.10, 8.60) and BTAS (3.18, 8.90) are lower than those of TAR<sup>17</sup> (6.23, 9.44) and TAS<sup>18</sup> (4.30, 10.06) respectively. This behaviour can be explained on the basis that, the fusion of a benzene ring to thiazole moiety decreases the  $pK_a$  values of the two investigated benzothiazolylazo phenol derivatives. This is in accordance with the view that the fusion of a benzene ring to 2-aminothiazole moiety decreases the  $pK_{NH}$  due to an increase in the resonance interactions involving the unshared pair of electrons of the nitrogen atom in thiazole. This is in accordance with an earlier observation that the fusion of a benzene ring decreases the  $pK_{NH}$  of pyridine from 5.23 to 4.94 in quinoline<sup>19</sup>.

Furthermore,  $pK_{a2}$  values of BTAS are higher than those of BTAR. This can be attributed to the ease of ionization of -COOH group in BTAS at lower pH values forming the monoanionic species of BTAS. This renders the ionization of the -OH group more difficult (i.e. higher  $pK_a$  values).

## References

- 1 Chromy V & Sommer L, *Talanta*, 14 (1967) 393.
- 2 Sommer L, Sepel T & Ivanov V M, *Talanta*, 15 (1968) 949.
- 3 Shibata S, *Chelates in analytical chemistry*, Vol. 4, edited by H A Flascka & A J Barnard (Jr) (Marcel Dekker, New York) 1972.
- 4 Hovinić H R, *Analyst*, 100 (1975) 769.
- 5 Garcia Montelongo F, Arias J J & Jimenez F, *Mikrochim Acta*, 11 (1983) 349.
- 6 Sanchez Ma J, Francisco F, Jimenez F & Garcia Montelongo F, *Talanta*, 36 (1989) 831.
- 7 Zhang C P, Qi D Y & Zhou T Z, *Talanta*, 29 (1982) 1119.
- 8 Pollard F H, Nicklers G, Samuelson T J & Anderson R J, *J Chromatogr*, 16 (1964) 231.
- 9 Vogel A I, *Practical organic chemistry*, 3rd Edn (Longmans, London) 1961.
- 10 Douheret G, *Bull Soc chim Fr* (1967) 1412.
- 11 Sommer L., Kuban V & Havel J, *Folia Fac Sci Nat Univ Brno Chemia*, 7 (1970) Part I, p. 33-62.
- 12 Rossotti F J C & Rossotti H, *Determination of stability constants* (McGraw-Hill, New York) 1961.
- 13 Kuban V, Sommer L & Havel J, *Colln Czech chem Commun*, 40 (1975) 604.
- 14 Kuban V & Havel J, *Acta chemica Scand*, 27 (1973) 528.
- 15 Sillen L G & Warnqvist B, *Ark Kemi*, 31 (1969) 377.
- 16 Coetzee J F & Richie C D, *Solute-solvent interactions* (Marcel Dekker, New York) 1969.
- 17 Sommer L & Ivanov Y M, *Talanta*, 14 (1967) 171.
- 18 Hafez O S, Ph.D. Thesis, Alexandria University, Faculty of Science (1990).
- 19 Albert A, Goldacre R & Philips J, *J chem Soc*, (1948) 2240.