Thermochimica Acta, 237 (1994) 357-368
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01700-Q

Thermodynamics of substituted rhodanine. Part 1. Temperature, medium and substituent effects on the dissociation constants of 3-benzamidorhodanine and its substituted derivatives

Ibrahim Shehatta [a,*] and A.A. El-Bindary [b]

[a] *Chemistry Department, Mansoura Faculty of Science, Mansoura University, Mansoura, Egypt*

[b] *Chemistry Department, Demiatta Faculty of Science, Mansoura University, Mansoura, Egypt*

(Received 4 October 1993; accepted 14 January 1994)

Abstract

The dissociation constants of 3-benzamidorhodanine and its substituted derivatives have been determined potentiometrically and spectrophotometrically. The data are discussed in terms of the electronic character of the substituents and of the change in temperature and medium of the solution. The pK^H values have been found to increase with increasing electron-repelling nature of the substituents and with decreasing ionic strength and dielectric constant of the medium. The resulting linear Hammett plots of pK^H versus the Hammett constant σ values indicates the coplanarity of the molecules of the investigated compounds. The dissociation constants have been found to depend on the nature of the solvent as well as on its content. The evaluated thermodynamic parameters indicate that the dissociation processes are non-spontaneous, endothermic, and entropically unfavourable. These functions are affected by the electronic character of the substituents.

INTRODUCTION

The importance of 3-benzamidorhodanine and its substituted derivatives in the inhibition of mycobacterium tuberculosis has been reported [1]. Although work on acid-base properties has received the attention of many workers, little attention has been paid to the acid-base properties of these particular ligands, despite their role in the biological field [2, 3]. Accordingly, in continuation of our studies on acid-base behaviour [4-7] and on the effects of the medium and temperature on dissociation processes [6], the present work presents a study of the effect of medium, temperature and substituent on the dissociation of these compounds. Thus, their pK^H values were determined potentiometrically in different compositions of aquo-

---

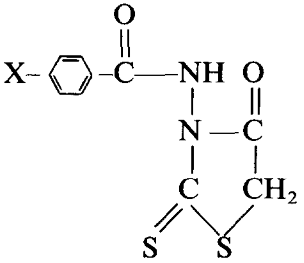
[*] Corresponding author.

organic mixtures and are discussed in terms of their molecular structures. These pK^H values were confirmed by a spectrophotometric technique. Furthermore, their thermodynamic dissociation parameters have been evaluated and are discussed.

EXPERIMENTAL

Preparation of 3-benzamidorhodanine and its substituted derivatives

The organic compounds (**I**) were prepared according to the method of Tadashi and Masaki [1]. The purity was checked and confirmed by elemental analysis and IR spectroscopy.



Compound (**I**). X is H (BR), $-NO_2$ (PNBR), $-Cl$ (PCBR), $-CH_3$ (PMBR) or $-OCH_3$ (PTBR).

Potentiometric measurements

The apparatus, general conditions and methods of calculation were the same as those reported in previous works [4, 5]. The pH-meter readings in different solvent compositions were corrected according to the Van Uitert and Hass relation [8]. The organic solvents were BDH extrapure (spectroscopic grade) and used without further purification.

Spectrophotometric measurements

The absorption spectra were recorded in the wavelength range 200–400 nm on a Perkin-Elmer (Lambda 2) spectrophotometer with a thermostatted cell-holder using 1-cm matched silica cells.

RESULTS AND DISCUSSION

Potentiometric studies

The average number of protons associated with the reagent molecule at different pH values, $\bar{n}_A$, was calculated from the titration curves of acid in

TABLE 1

Thermodynamic functions for the dissociation of 3-benzamidorhodanine and its derivatives in 20% (v/v) ethanol–water mixture and 0.1 M KCl

Comp.	Temp. in K	Dissociation constant [a]		Free energy in kJ mol^{-1}		Enthalpy change in kJ mol^{-1}		Entropy change in J K^{-1} mol^{-1}	
		pK_1	pK_2	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
PNBR	298.15	6.76	9.23	38.59	52.69				
	308.15	6.63	9.04	39.12	53.34	21.81	38.09	56.3	49.2
	318.15	6.52	8.81	39.72	53.67				
PCBR	298.15	7.45	10.31	42.53	58.86				
	308.15	7.31	10.08	43.13	59.47	22.72	39.06	66.4	66.3
	318.15	7.20	9.88	43.86	60.19				
BR	298.15	7.70	10.70	43.97	61.08				
	308.15	7.56	10.50	44.61	61.95	23.62	39.90	68.2	71.2
	318.15	7.44	10.26	45.32	62.50				
PMBR	298.15	7.94	11.02	45.33	62.91				
	308.15	7.80	10.81	46.02	63.78	23.62	39.92	72.8	77.2
	318.15	7.68	10.58	46.78	64.45				
PTBR	298.15	8.10	11.20	46.24	63.94				
	308.15	7.95	10.96	46.91	64.67	24.54	40.88	72.7	77.3
	318.15	7.83	10.75	47.70	65.49				

[a] ±(0.03–0.05).

the presence and absence of rhodanine compounds. Thus, the formation curves ($\bar{n}_A$ versus pH) for the proton–ligand systems were constructed and found to extend between 0 and 2 for the rhodanine derivatives in the $\bar{n}_A$ scale. This means that these compounds have two dissociable protons (the enolized hydrogen ion of the carbonyl oxygen in the rhodanine ring and the amidic proton, CONH). These curves could be utilized to obtain the protonation constants, $\log K_1^H$ and $\log K_2^H$, by interpolation at $\bar{n}_A = 0.5$ and 1.5, respectively. These values were confirmed by different computational methods [4, 9], namely, half $\bar{n}$, least-squares fitting, mid-point and successive approximation. The average values obtained are listed in Table 1.

Substituent effect on pK^H

An inspection of the results in Table 1 reveals that the pK^H values of BR and its substituted derivatives appear to be affected by the substituent (X). The p-OCH_3 and p-CH_3 derivatives (PTBR and PMBR) have a lower acidic character (higher pK^H values) than the p-Cl and p-NO_2 derivatives (PCBR and PNBR). This is quite reasonable because the presence of p-OCH_3 and p-CH_3 groups will enhance the electron density by their high positive mesomeric and positive inductive effects, respectively, whereby stronger N–H and O–H bonds are formed. The presence of electron-withdrawing groups (p-NO_2 and p-Cl) will lead to the opposite effect. Therefore, the electron-repelling properties of the methoxy and methyl groups retard the removal of the ligand protons and hence increase the basicity of the ligands, while the reverse happens for the electron-acceptor groups (NO_2 and Cl). Thus, the pK_1^H and pK_2^H values for BR and its substituted derivatives at constant temperature, solvent composition and ionic strength, follow the sequence PTBR > PMBR > BR > PCBR > PNBR.

In an attempt to correlate quantitatively the dissociation constants of BR and its substituted derivatives with the substituent (X), the Hammett equation was applied

$$pK_X^H = pK_0^H + \rho\sigma_X \tag{1}$$

where pK_X^H and pK_0^H are the dissociation constants of the substituted and unsubstituted derivatives, respectively, ρ is the reaction constant and σ_X is the Hammett constant.

Straight lines are obtained on plotting pK_1^H or pK_2^H values at different temperatures, solvent compositions and ionic strengths, versus σ_X (Fig. 1 is a representative example). The slope and intercept values of these lines are calculated statistically using the linear regression method and are given in Table 2. Because the points drawn in Fig. 1 did not deviate from the most probable straight line by more than the experimental error (correlation coefficients in all cases ≈ 1), the pK^H values of BR and its substituted derivatives correlate well with σ, the Hammett constant. This means that the para-substituents in the phenyl moiety have a direct influence on the pK^H values of the investigated compounds, revealing the coplanarity of the molecule, and thus affording a maximum resonance via delocalization of its π-system.

Moreover, a good agreement between the derived pK^H values (intercepts) and the experimental values for the unsubstituted derivative (BR) is obtained (Table 2). The negative values of the slope (ρ) are an indication of the increased acidity of the dissociable protons on increasing the acceptor character of the substituent (X). Moreover, these reaction constants increase with decreasing dielectric constants (Table 2) in accordance with relation (2) observed for acid dissociation constants of phenol [10] and carboxylic acids [11]

$$\rho = \left(\frac{B_1}{D} + B_2\right) \Big/ RTd^2 \tag{2}$$

where D is the dielectric constant of the medium

Ionic strength and dielectric constant effects on pK^H

As expected, the study of the dependence of pK^H values on ionic strength (Table 3) showed that there is a regular, slow decrease in the values of pK^H with increasing ionic strength of the medium, in accordance with the Debye–Hückel equation [12].

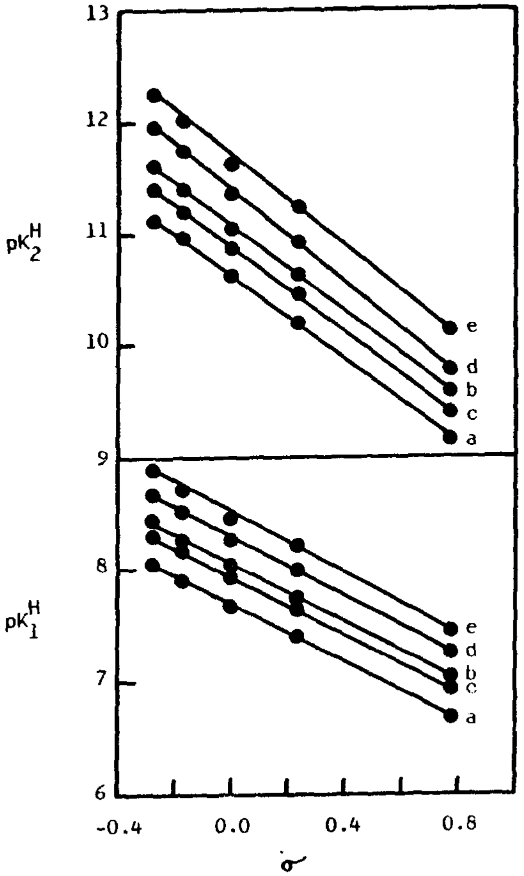


Fig. 1. Correlation of pK_1^H and pK_2^H with the Hammett constant σ at 298.15 K in (a), pure water; (b), 50% (v/v) ethanol–water; (c), 50% methanol–water; (d), 50% acetone–water; and (e), 50% dioxane–water mixtures.

However, the observed increase in pK^H values (Table 4, Fig. 2) as the content of the organic co-solvent in the medium is increased can be attributed to [13]: (i) the increase in proton solvation, (ii) the decrease in the dielectric constant of the medium, and (iii) the decrease of the extent of hydrogen bonding by the organic solvent. This can be explained as follows. Suppose a monoprotic ligand (HL) dissociates according to the equilibrium

$$HL \rightleftharpoons H^+ + L^-$$

Therefore, its dissociation constant in pure aqueous medium, $\log K_w^H$, is related to that in an aquo–organic mixture, $\log K_s^H$, by the following [14]

$$\log K_w^H = \log K_s^H + \log \frac{\gamma_{H^+}\gamma_{L^-}}{\gamma_{HL}} \tag{3}$$

TABLE 2

Statistical data for 3-benzamidorhodanine and its substituted derivatives in different ionic strengths and solvents at various temperatures (correlation coefficients in all cases ≈1)

Solvent	%	KCl in M	Temperature in K	pK_1^H			pK_2^H		
				Exp. [a]	Calc. [b]	$-\rho$ [c]	Exp. [a]	Calc. [b]	$-\rho$ [c]
Ethanol	20	0.05	298.15	7.85	7.86	1.294	10.95	10.88	1.932
Ethanol	20	0.10	298.15	7.70	7.73	1.260	10.70	10.71	1.879
Ethanol	20	0.10	308.15	7.56	7.58	1.235	10.50	10.49	1.848
Ethanol	20	0.10	318.15	7.44	7.47	1.234	10.26	10.27	1.853
Ethanol	20	0.15	298.15	7.61	7.64	1.275	10.48	10.52	1.875
Ethanol	20	0.20	298.15	7.54	7.55	1.299	10.31	10.33	1.874
Ethanol	40	0.10	298.15	7.91	7.94	1.300	10.93	10.95	1.912
Ethanol	50	0.10	298.15	8.01	8.05	1.304	11.05	11.08	1.921
Ethanol	60	0.10	298.15	8.10	8.14	1.332	11.14	11.18	1.935
Ethanol	70	0.10	298.15	8.20	8.24	1.340	11.28	11.31	1.914
Methanol	50	0.10	298.15	7.88	7.93	1.272	10.85	10.87	1.870
Acetone	50	0.10	298.15	8.25	8.29	1.343	11.36	11.39	2.070
1,4-Dioxane	50	0.10	298.15	8.46	8.50	1.357	11.63	11.68	2.015

[a] Potentiometrically. [b] Calculated using the Hammett equation. [c] Slope of the Hammett equation.

where γ is the activity coefficient of the subscripted species in the aquo–organic solvent relative to that in pure water medium.

With increasing amount of organic solvent, the dielectric constant of the medium decreases, and thus the activity coefficients of the charged species (H^+ and L^-) increase [14]. Consequently, according to eqn. (3), $\log K_s^H$ will decrease, i.e. higher pK_s^H values are to be expected.

The dependence of pK^H on the dielectric constant is given by the relation [15]

TABLE 3

Acid dissociation constants ($pK^H \pm (0.04–0.08)$) for 3-benzamidorhodanine and its derivatives in different concentrations of KCl at 298.15 K and 20% (v/v) ethanol–water mixture

KCl in M	PNBR		PCBR		BR		PMBR		PTBR	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
0.20	6.52	8.85	7.29	9.95	7.54	10.31	7.74	10.64	7.90	10.82
0.15	6.62	9.05	7.38	10.14	7.61	10.48	7.83	10.85	7.98	11.02
0.10	6.76	9.23	7.45	10.31	7.70	10.70	7.94	11.02	8.10	11.20
0.05	6.88	9.34	7.51	10.47	7.85	10.95	8.08	11.17	8.24	11.35
0.00 [a]	7.25	10.04	7.73	11.01	8.15	11.59	8.42	11.72	8.60	11.90

[a] These values were obtained by linear regression of pK^H versus $\mu^{1/2}$.

TABLE 4

Acid dissociation constants pK^H and free energies of transfer $\Delta_w^s G$ (kJ mol^{-1}) for 3-benzamidorhodanine and its derivatives in various aquo-organic mixtures at 298.15 K and 0.1 M KCl

	Solvent composition in % (v/v)								
	Ethanol						Methanol	Acetone	1,4-Dioxane
	0[a]	20	40	50	60	70	50	50	50
PNBR									
pK_1	6.70	6.76	6.94	7.04	7.11	7.21	6.95	7.25	7.44
pK_2	9.15	9.23	9.45	9.58	9.67	9.82	9.41	9.77	10.12
$\Delta_w^s G_1$	–	0.34	1.37	1.94	2.34	2.91	1.43	3.14	4.22
$\Delta_w^s G_2$	–	0.46	1.71	2.45	2.97	3.82	1.48	3.54	5.54
PCBR									
pK_1	7.39	7.45	7.65	7.76	7.85	7.93	7.65	8.00	8.21
pK_2	10.23	10.31	10.55	10.67	10.77	10.90	10.48	10.96	11.22
$\Delta_w^s G_1$	–	0.34	1.48	2.11	2.63	3.08	1.48	3.48	4.68
$\Delta_w^s G_2$	–	0.46	1.83	2.51	3.08	3.82	1.43	4.17	5.65
BR									
pK_1	7.64	7.70	7.91	8.01	8.10	8.20	7.88	8.25	8.46
pK_2	10.62	10.70	10.93	11.05	11.14	11.28	10.85	11.36	11.63
$\Delta_w^s G_1$	–	0.34	1.54	2.11	2.63	3.20	1.37	3.48	3.68
$\Delta_w^s G_2$	–	0.46	1.77	2.45	2.97	3.77	1.31	4.22	5.77
PMBR									
pK_1	7.87	7.94	8.16	8.26	8.37	8.47	8.14	8.51	8.71
pK_2	10.94	11.02	11.27	11.41	11.51	11.66	11.20	11.74	12.02
$\Delta_w^s G_1$	–	0.40	1.66	2.23	2.85	3.43	1.54	3.65	4.80
$\Delta_w^s G_2$	–	0.46	1.88	2.68	3.25	4.11	1.48	4.57	6.17
PTBR									
pK_1	8.04	8.10	8.32	8.43	8.52	8.63	8.31	8.68	8.89
pK_2	11.13	11.20	11.46	11.60	11.71	11.82	11.37	11.95	12.25
$\Delta_w^s G_1$	–	0.34	1.60	2.23	2.74	3.37	1.54	3.65	3.85
$\Delta_w^s G_2$	–	0.40	1.88	2.68	3.31	3.94	1.37	4.68	6.39

[a] These values were obtained by linear regression of pK^H versus ethanol mole fraction.

$$pK_s^H = pK_w^H + \frac{0.43Ne^2}{RT}\frac{z_1 z_2}{r_1 r_2}\left(\frac{1}{D}\right) \qquad (4)$$

where z_1 and z_2 are the charges carried by the ions in equilibrium, r_1 and r_2 are the radii of the ions, N is Avogadro's number and e is the electron charge. Therefore, pK_s^H versus $1/D$ plots should be linear, where D is the dielectric constant of the medium. However, the slight deviation from linearity (Fig. 3) reveals that the other two factors, apart from the electrostatic factor resulting from the variation in the dielectric constant, affect the dissociation process.

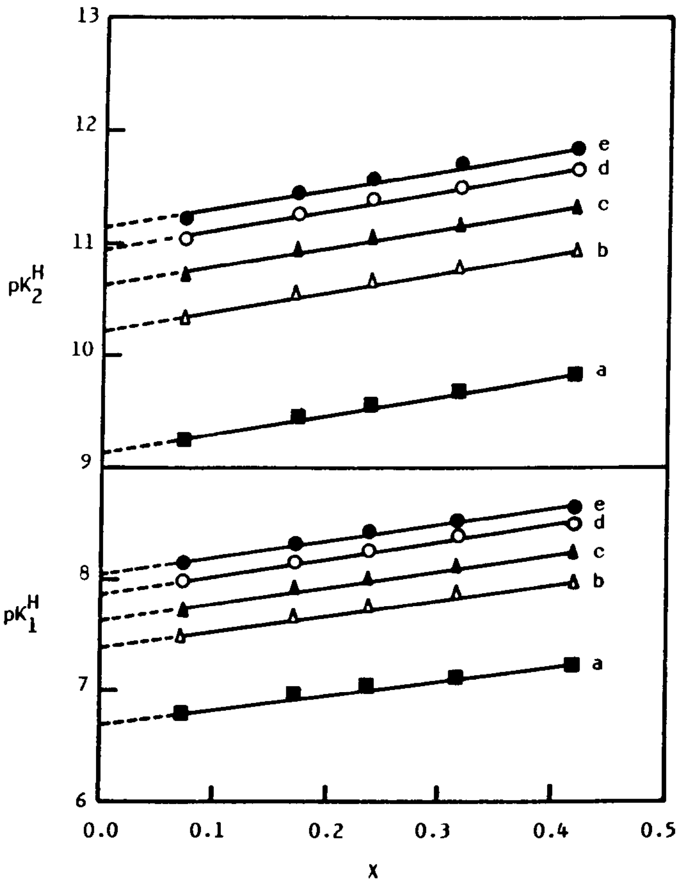


Fig. 2. Dependence of pK_1^H and pK_2^H on the mole fraction of the ethanol present in ethanol–water medium at 298.15 K for (a), PNBR; (b), PCBR; (c), BR; (d), PMBR; and (e), PTBR.

Therefore, because water molecules form hydrogen bonds more than other solvents [16], the conjugate base L^- will interact less through hydrogen bonds with solvent molecules as the amount of organic co-solvent is increased, i.e. it is less stable. Thus, the γ_{A^-} values increase and the pK_s^H values decrease according to eqn. (3).

As shown in Table 4 for a particular composition (50% v/v) of the organic solvent–water mixture, the pK^H values for the investigated compounds decrease dioxane–water > acetone–water > ethanol–water > methanol–water, which is in agreement with the $1/D$ values and inversely proportional to the hydrogen-bonding ability of the solvents [16].

Moreover, the more the solvent accepts a proton, the more the ligand acid dissociates. The order of basicities of the pure solvent molecules is water > dioxane > ethanol > acetone [17]. This order does not exactly follow the dissociation constant order (Table 3). Therefore, the variation of

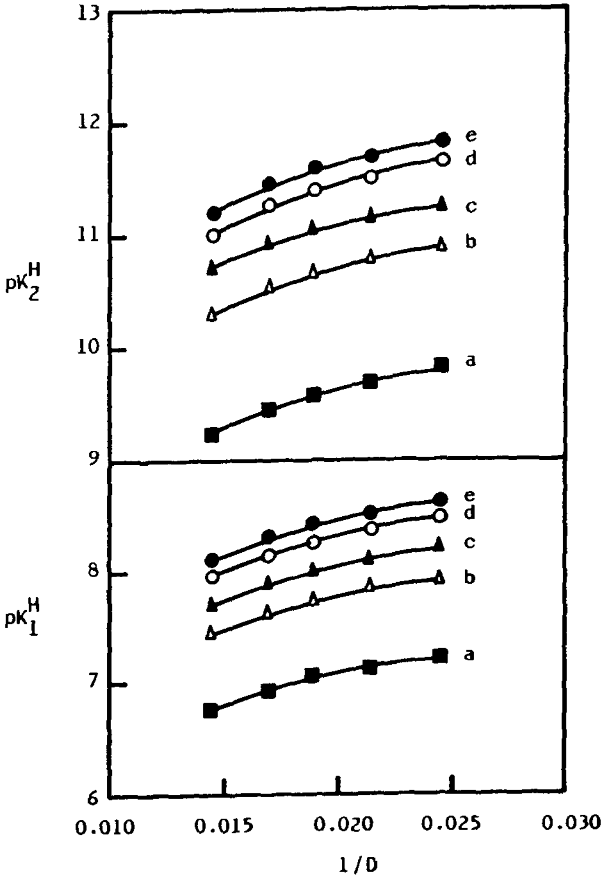


Fig. 3. Dependence of pK_1^H and pK_2^H on the dielectric constant of ethanol–water mixtures at 298.15 K for (a), PNBR; (b), PCBR; (c), BR; (d), PMBR; and (e), PTBR.

the pK^H values is mainly dependent on the dielectric constant of the medium. In other words, the dielectric constant factor is the overcoming and predominant among the above-mentioned factors.

Also, ion–solvent interactions are important in accounting for acid–base equilibria [18]. The observed changes in the standard molar Gibbs free energy of transfer from water (w), as reference solvent, to aquo–organic solvents (s) were calculated from

$$\Delta_w^s G = 2.303RT\Delta pK^H = 2.303RT[pK_s^H - pK_w^H] \qquad (5)$$

The calculated transfer free energies are given in Table 4. Inspection reveals that these values are positive in all solvent compositions, suggesting that the transfer of ions from water to aquo–organic solvents is not favourable. Furthermore, the increase in $\Delta_w^s G$ with increasing ethanol content indicates that the hydrogen ion, stabilized by solvation with water molecules, i.e. the proton, interacts with water molecules more than with ethanol molecules in ethanol–water solvents. Furthermore, the order of $\Delta_w^s G$ values for 50% (v/v) aquo–organic solvents is exactly the same as that for the pK^H values, which confirms the above theory.

Temperature effect and thermodynamic parameters

To obtain information about the dependence of the dissociation constants of BR and its derivatives on temperature, the pK^H values were calculated at 298.15, 308.15 and 318.15 K and are listed in Table 1. The corresponding thermodynamic functions (ΔG, ΔH and ΔS) were evaluated using the relation

$$\Delta G = 2.303RTpK^H = \Delta H - T\Delta S \tag{6}$$

The slopes and intercepts of the ΔG versus T plots provide the $-\Delta S$ and ΔH values for the dissociation, respectively. Moreover, the slopes of pK^H versus $1/T$ plots could be utilized to evaluate the enthalpy change. All these values are reported in Table 1. From these results the following conclusions can be made.

(a) The pK^H values decrease with increasing temperature, i.e. the acidity of the ligands increases, independent of the nature of the substituent.

(b) The ΔG values for the dissociation of BR and its derivatives are positive and increase with increasing electron-repelling character of the substituent (X). This reveals that the dissociation process is non-spontaneous and increases with an increase in the electron-acceptor character of the substituent.

(c) The positive value of the enthalpy of dissociation of BR and its derivatives indicates that such a process is endothermic and increases with increasing temperature. Moreover, the constant value for the enthalpy change ($\Delta H_1 = 23.26 \pm 1.43$ and $\Delta H_2 = 39.57 \pm 0.51$ kJ mol^{-1}) confirms that the entropy term ΔS contributes significantly to the free energy change ΔG.

(d) The dissociation processes for BR and its derivatives have negative ΔS values due to increased order as a result of the solvation processes. Furthermore, the order increases as the electron-repelling nature of the substituent increases.

(e) The correlations of pK^H values versus $1/T$ are linear in all cases, suggesting that the ΔC_p values for the dissociation processes are zero [4] over the studied temperature range (298.15–318.15 K).

Spectrophotometric studies

The electronic absorption spectra of 3-benzamidorhodanine and its derivatives have been studied in absolute ethanol. The spectrum of each compound shows two bands. The first (A) observed in the 231–251 nm

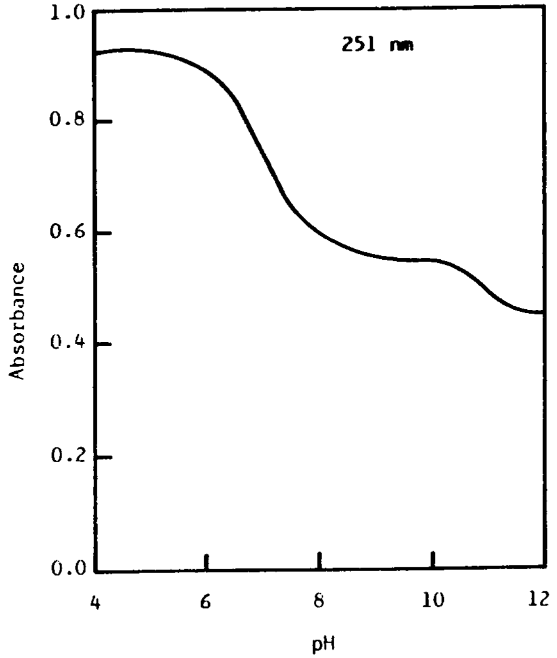


Fig. 4. Absorption–pH curve for BR in 20% (v/v) ethanol–water mixture at 298.15 K.

region can be assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic system and its conjugation. The second (B) in the 287–295 nm region is less intense and corresponds to the $n \rightarrow \pi^*$ transition of the carbonyl and thiocarbonyl groups [19].

The spectra of BR (5×10^{-5} M) were studied in 20% (v/v) ethanolic Britton–Robinson buffer solutions of varying pH values. Increasing the pH leads to a decrease in absorbance until a constant value is reached at pH 9.5. The bands at 251 and 292 nm exhibit a red shift as a result of the ionization of the OH group (in the rhodanine moiety). At pH values higher than 9.5, the absorbance decreases and it reaches a constant value at 11.5. The last change is due to the dissociation of the hydrazo group [7] of BR from the mono-ionized to the di-negative ion.

The absorption spectra of BR and its derivatives are characterized by the presence of two isosbestic points at ≃230 and 265 nm, suggesting the existence of two acid–base equilibria between the two forms existing in solution

$$H_2L \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} HL^- \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} L^{2-}$$

The absorbance–pH curves at 251 nm (Fig. 4 is a representative example) are typical dissociation curves supporting the hypothesis of an acid–base equilibrium. Therefore, the variation of absorbance with pH is utilized to determine the mean values of pK_1^H and pK_2^H using the different spectrophotometric methods [20]. The evaluated pK_1^H and pK_2^H values are found to be in fair agreement with those obtained potentiometrically within an error of $\leq 3\%$. The change in medium in the two techniques may be the reason for the marginal change in the dissociation constants.

In conclusion, the increase in temperature and in the electron-acceptor character of the substituent enhance the dissociation processes of 3-benzamidorhodanine and its substituted derivatives. However, their pK^H values decrease with increasing ionic strength and organic content of the media. These processes are non-spontaneous, endothermic, and entropically unfavourable, as suggested by the derived thermodynamic functions. The substituents have no effects on the enthalpy of dissociation, while their effects on the free energy change and the order of the system are pronounced.

REFERENCES

1 S. Tadashi and O. Masaki, J. Pharm. Soc. (Jpn.), 75 (1955) 1535.
2 F.C. Brown, C.K. Bradsher, E.C. Morgan, M. Tetenbaum and P. Wilder, J. Am. Chem. Soc., 78 (1956) 384.
3 F.C. Brown, C.K. Bradsher, B.F. Moser and S. Forrester, J. Org. Chem., 24 (1959) 1056.
4 I. Shehatta, M.N.H. Moussa and M. Hafez, Thermochim. Acta, 219 (1993) 121.
5 A.A. El-Bindary, I. Shehatta and E.M. Mabrouk, Monatsh. Chem., in press.
6 I. Shehatta, Z. Phys. Chem. N.F., in press.
7 A.A. El-Bindary, Monatsh. Chem., in press.
8 L.G. Van Uitert and C.G. Hass, J. Am. Chem. Soc., 75 (1953) 451.
9 M.T. Beck and I. Nagybal, Chemistry of Complex Equilibria, John Wiley, New York, 1990.
10 J. Corse and L.L. Ingraham, J. Am. Chem. Soc., 73 (1951) 5706.
11 J.D. Roberts and E.A. McElhill, J. Am. Chem. Soc., 72 (1950) 628.
12 J.T. Edsall and J. Wyman, Biophysical Chemistry, Vol. 1, Academic Press, New York, 1958, p. 442.
13 N. Kole and A.K. Chaudhury, J. Inorg. Nucl. Chem., 43 (1981) 2471.
14 J.F. Coetzee and C.D. Ritchie, Solute–Solvent Interactions, Marcel Dekker Ltd., New York, London, 1969, p. 221, 222.
15 G. Chartar and B. Tremillon, Chemical Reaction in Solvents and Melts, Pergamon Press, New York, 1969, p. 306.
16 F. Franks and D.J.G. Ives, Quart. Rev., 20 (1966) 1.
17 E.A. Braude, J. Chem. Soc., (1948) 1971.
18 D. Feakins, in F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann, London, 1969.
19 K.M. Ibrahim, A.M. Shallaby, A.A. El-Bindary and M.M. Mostafa, Polyhedron, 5(5) (1986) 1105.
20 R.M. Issa, H. Sadek and I.I. Izzat, Z. Phys. Chem. N.F., 74 (1971) 17.