

Thermodynamics of the Complexation of Some Transition Metal Ions with Trithiocarbodiglycolic Acid. Potentiometric and Voltammetric Studies

A. A. El-Bindary^{1,*}, I. S. Shehatta², and E. M. Mabrouk³

¹ Chemistry Department, Faculty of Science, Mansoura University, Demiatta, Egypt

² Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

³ Chemistry Department, Faculty of Science, Zagazig University, Benha, Egypt

Summary. Proton-ligand dissociation and metal-ligand stability constants of trithiocarbodiglycolic acid (*TCGA*) with some transition metal ions were calculated potentiometrically. The order of stability constants was found to be $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. The effect of temperature on the stability of the complexes formed was studied and the corresponding thermodynamic functions were derived and discussed. Polarographic and cyclic voltammetric behaviours of *TCGA* were investigated in B.R. buffer solutions of *pH* 2–12. In solutions of *pH* < 8, the polarograms and cyclo-voltammograms exhibited a single 2-electron diffusion-controlled irreversible step, corresponding to the reduction of the C=S. The mechanism of the reduction process was postulated and the kinetic parameters of the electrode process were evaluated.

Keywords. Trithiocarbodiglycolic acid; Dissociation and stability constants; Thermodynamics; Potentiometry; Polarography; Cyclic-voltammetry.

Thermodynamik der Komplexierung einiger Übergangsmetallionen mit Trithiocarbodiglykolsäure. Potentiometrische und voltammetrische Untersuchungen

Zusammenfassung. Die Protonendissoziation vom Liganden und die Metall-Ligand-Stabilitätskonstanten von Trithiocarbodiglykolsäure (*TCGA*) mit einigen Übergangsmetallionen wurden potentiometrisch bestimmt. Die Reihung der Stabilitäten ist $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. Die Temperaturabhängigkeit der Stabilitäten wurde gemessen und die entsprechenden thermodynamischen Funktionen abgeleitet. Das polarographische und cyclovoltammetrische Verhalten von *TCGA* wurde in B.R.-Puffer bei *pH* 2–12 ermittelt. In Lösungen von *pH* < 8 zeigten die Polarogramme und Cyclovoltagramme eine einzelne diffusionskontrollierte irreversible 2-Elektronen-Stufe, die der Reduktion von C=S entspricht. Es wurde ein Mechanismus postuliert und die kinetischen Parameter des Elektrodenprozesses wurden bestimmt.

Introduction

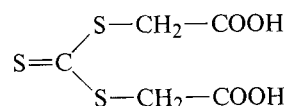
The importance of metal ions in biological processes has been cited [1]. In the last decade, there is growing interest in the formation of binary and ternary complexes involving ligands containing functional groups such as –COOH present in enzymes. These complexations occur ordinary in biological fluids where the potential

ligands compete for metal ions in vivo, i.e., Na, K, Mg, Ca, Mn, Fe, Co, Cu and Zn. Moreover, the inhibition of *Mycobacterium tuberculosis* [2] by sulphur containing compounds is of utmost importance. In previous work different tools, e.g. calorimetry [3,4], potentiometry [5], spectroscopy [6], cyclic voltammetry [7], and polarography [8], were used to evaluate the stability constants and the corresponding thermodynamic functions of the complexes formed in solution. Accordingly, in the present study we set out to determine the stability constants of the binary complexes of trithiocarbodiglycolic acid (*TCGA*) with Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} . The effect of temperature has been studied and the thermodynamic parameters have been calculated and discussed. The study extended to throw some light on the reduction mechanism of *TCGA* at the mercury electrode since no voltammetric studies has been made for this compound.

Experimental Part

Synthesis of *TCGA*

TCGA (structure 1) was prepared by bubbling hydrogen sulfide through a KOH solution (63 g KOH/100 ml dist. H_2O) with a constant stirring for 1/2 h followed by further addition of KOH (63 g) until all the solid was dissolved. Carbon disulphide (76 g) was added and the mixture was stirred vigorously for 2 h till a dark-red solution of potassium thiocarbonate was formed. Finally, potassium chloroacetate was added portionwise to the dark-red solution, and the reaction mixture was stirred at 40°C for 4 h. On acidifying with conc. HCl a pale-yellow precipitate was formed. The isolated compound was filtered off, washed with ice water and recrystallized from water, m.p. $164 \pm 1^\circ\text{C}$ (M.W. 226.1). Its purity was checked by elemental analysis (found: C 26.55, H 2.65; calcd.: C 26.56, H 2.67).



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Reagents and Materials

Metal ion solutions (0.001 M) were prepared from AnalaR metal chloride samples (BDH) in bi-distilled water and standardized with *EDTA*. The ligand solution (0.01 M) was prepared by dissolving the accurate weight of the solid in ethanol (AnalaR). Solutions of 0.01 M HCl and 1 M KCl were also prepared in bi-distilled water. A carbonate-free sodium hydroxide solution in 20% (v/v) ethanol-water was used as titrant and standardized against AnalaR oxalic acid.

Apparatus and Procedures

The pH-meter readings were measured to 0.01 unit with Orion Research model 601A/Digital Ionalyzer standardized before and checked after each titration with buffer solutions produced by Fisher (New Jersey, U.S.A.). The following mixtures were prepared and titrated potentiometrically at 298.15 K against standard 0.02 M NaOH in 20% (v/v) ethanol-water:

1. 5 ml 0.01 M HCl + 5 ml 1 M KCl + 10 ml ethanol.

2. 5 ml 0.01 M HCl + 5 ml 1 M KCl + 5 ml ethanol + 5 ml 0.01 M TCGA.
3. 5 ml 0.01 M HCl + 5 ml 1 M KCl + 5 ml ethanol + 5 ml 0.01 M TCGA + 5 ml 0.01 M metal chloride.

For each mixture the volume was made up to 50 ml with bi-distilled water before the titration. These titrations were repeated for temperatures of 288.15 and 308.15 K. A constant temperature was adjusted to ± 0.05 K by using an ultrathermostate (Kotterman 4130, Germany).

For converting the *pH*-meter reading (*B*) in 20% (*v/v*) ethanol–water and 0.1 M KCl to $[H^+]$ values, the equation of Van Uitert and Hass [9] was applied,

$$-\log [H^+] = B + \log U_H$$

where $\log U_H$ is the correction factor for the solvent composition and ionic strength for which *B* is read. To obtain $\log U_H$, values of *B* were recorded on a series of solutions containing known concentrations of HCl and sufficient KCl to give a constant ionic strength of 0.1 M. The relation drawn between the decadic logarithm of the known hydrogen ion concentrations and the corresponding values of *B* was utilized to estimate the correction factor which equals the intercept of this plot and was found to be equal -0.09 .

The dc- and dp-polarograms were recorded using a Metrohm E506 polarecord with a polarography stand E505 DC. The capillary possessed the following characteristics: *m* = 1.66 mg/sec, *t* = 4.5 sec/drop for mercury height (*h*) = 100 cm in 0.1 M KCl solution (open circuit). All polarograms were recorded using a saturated Ag/AgCl electrode as reference electrode with platinum wire as auxiliary electrode. A polarographic analyzer model 246A was used for cyclic voltammetry measurements. Its electrode assembly model 303A consists of a hanging mercury drop electrode of area 0.026 cm² (working electrode), a platinum wire (counter electrode) and Ag/AgCl (reference electrode). All voltammetric measurements were made at a temperature of 298.15 K. Statistical treatment of the data was carried out using the IBM PC (5.1) disk operating system.

Results and Discussion

Potentiometric Studies

Proton-Ligand Stability Constants

TCGA is a weak acid due to the presence of two carboxyl groups. The protons associated with the ligand naturally dissociate in two steps in solution which correspond to the two dissociable constants of the ligand. In order to determine these constants, the Calvin-Bjerrum technique as adapted by Irving and Rossotti [10] was employed. For that, the titration curves of acid in presence and absence of TCGA were used.

The proton-ligand formation number, \bar{n}_A , was calculated by the method of Irving and Rossotti [10] and used to draw the proton-ligand formation curve. Various computational methods [11, 12] were applied to determine the values of the stepwise proton-ligand stability constants, consequently the mean of the dissociation constants are given in Table 1. Inspection of these values reveals that $\Delta pK^H \simeq 3$. This high ratio between first and second dissociation constants exhibited by TCGA (dibasic acid) can be explained mainly on the basis of increased electrostatic interaction between the carboxyl groups and the formation of an intramolecular hydrogen bond in the acid ion [13]. In all such dibasic acids the geometry of the molecule is such as to allow the carboxyl groups to be oriented in close proximity to each other in order that these effects will operate effectively. These hydrogen bonds have been proven by infrared and nmr spectra for the acid ions of some acid

Table 1. Thermodynamic functions for the ionization of *TCGA* in 20% (*v/v*) ethanol–water and 0.1 *M* KCl

Temperature (K)	Dissociation constant		Free energy change (kJ mol ⁻¹)		Enthalpy change (kJ mol ⁻¹)		Entropy change (JK ⁻¹ mol ⁻¹)	
	<i>pK</i> ₁	<i>pK</i> ₂	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
288.15	4.07	6.92	22.46	38.73				
298.15	4.00	6.82	22.83	39.50	12.74	18.68	33.77	67.77
308.15	3.92	6.70	23.13	40.12				

maleate ion [14] (ΔpK in water 4.42 [15] and in 50% by weight ethanol–water 6.6 [13]) and for highly alkylated succinic acids [16] (ΔpK values between 6.6 and 9.5 in 50% by weight ethanol–water [13]).

Metal-Ligand Stability Constants

The values of the metal ligand formation number, \bar{n} , at different *pH* values were obtained and used to calculate the corresponding values of free-ligand exponent, *pL*, according to Irving and Rossitti [10]. Thus, the formation curves can be obtained by plotting \bar{n} versus *pL*. These curves were analyzed and various computational methods were applied to determine the stepwise metal-ligand stability constants. These calculated constants using different methods agree within 0.5% error. Accordingly the average values are represented in Table 2.

The following general remarks can be pointed out:

- (i) The maximum value of \bar{n} was $\simeq 2$ indicating the formation of both ML and ML₂ complexes.
- (ii) For all the complexes formed $\log K_1 > \log K_2$ because the vacant sites of the metal ions are more freely available for the binding of a first ligand than for a second one.
- (iii) The order of stability constants of the metal complexes of *TCGA* was found to be $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. This order is in a good agreement with the order observed by Mellor and Maley [17] and by Irving and Williams [18].

Effect of Temperature

An attempt was made to study the effect of temperature on both stepwise protonation constants of *TCGA* and the stepwise stability constants of its complexes with Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} . The different protonation and stability constants at 288.15, 298.15 and 308.15 K have been calculated (Tables 1 and 2). The corresponding thermodynamic parameters (ΔG , ΔH and ΔS) were evaluated using the following relationships:

$$\Delta G = -2.303 RT \log K,$$

Table 2. Thermodynamic functions at 298.15 K and stepwise stability constants for ML and ML₂ complexes at different temperatures

Cation	Temperature, K		log K ₁		log K ₂		Free energy change (kJ mol ⁻¹)		Enthalpy change (kJ mol ⁻¹)		Entropy change (JK ⁻¹ mol ⁻¹)	
	288.15	298.15	log K ₁	log K ₂	log K ₁	log K ₂	-ΔG ₁	-ΔG ₂	-ΔH ₁	-ΔH ₂	ΔS ₁	ΔS ₂
Fe ³⁺	8.23	6.14	8.13	6.00	8.01	5.85	46.41	34.25	18.68	24.63	93.00	32.14
Cu ²⁺	7.52	5.46	7.41	5.31	7.27	5.18	42.30	30.31	21.22	23.81	70.48	21.87
Ni ²⁺	7.00	4.85	6.87	4.73	6.77	4.60	39.22	27.00	19.57	21.23	66.04	19.23
Co ²⁺	6.78	4.65	6.67	4.51	6.55	4.40	38.08	25.75	19.52	21.30	62.14	15.08

$$d \log K/d(1/T) = \Delta H/2.303 R,$$

$$\Delta S = (\Delta H - \Delta G)/T.$$

All these parameters are listed in Tables 1 and 2. Examination of these values shows that:

- (i) The dissociation constants increase with the increase of the temperature revealing that the acidity of the ligand increases with increasing temperature. However, the stepwise stability constants for the complexes decrease with the rise of temperature indicating that the complexation process is favourable at lower temperature.
- (ii) The positive value of ΔG for the dissociation process suggests a non spontaneous nature of such process. While the chelation has a spontaneous character and it is favourable at lower temperatures where ΔG values for complexes formed are negative.
- (iii) The positive values of ΔH for the dissociation process follows the general pattern for ionization processes for acids: strong acids have slightly negative heat of ionization values, weak acids values close to zero, and very weak acids pronounced endothermic heats of ionization. On the other hand the complexation processes have negative ΔH values. This means that these processes are exothermic and favourable at lower temperatures.
- (iv) The dissociation process has a negative value for entropy change. This is due to increased order as a result of solvation process, i.e., the sum total of the bound solvent molecules with the dissociated ligand is more than that originally accompanying the undissociated form. Moreover, the second ionization process is accompanied by a larger negative entropy change than the first one as expected for the dicarboxylic acids [19]. But, the positive entropy change for complexation reaction confirms that complex formation is entropically favourable. This may be due to the ordered arrangement of the solvent around the ligand and metal ion is lost when the complex is formed.

Voltammetric Studies

DC-Polarography

The polarographic behaviour of $2.22 \times 10^{-4} M$ of TCGA was investigated in Britton-Robinson buffer solutions of pH 2–11 containing 20% (*v/v*) ethanol–water mixture. The polarograms were recorded at 298.15 K and are illustrated in Fig. 1. As shown in Fig. 1, the polarograms within the pH range 2–7 are consisting of a single reduction wave (A) with limiting current corresponding to the uptake of 2 electrons per molecule as indicated later from coulometry measurements. On increasing the pH of the solution up to pH 11 the limiting current of wave (A) decreases gradually and another more cathodic wave (A') is observed. The polarograms within the pH range 8–11 seemed to be consisting of two waves A and A'.

The half wave potential ($E_{1/2}$) of the polarographic wave shifted to more negative values on increasing the pH of the solution, denoting that hydrogen ions are consumed in the reduction process [20]. On plotting the $E_{1/2}$ values versus the

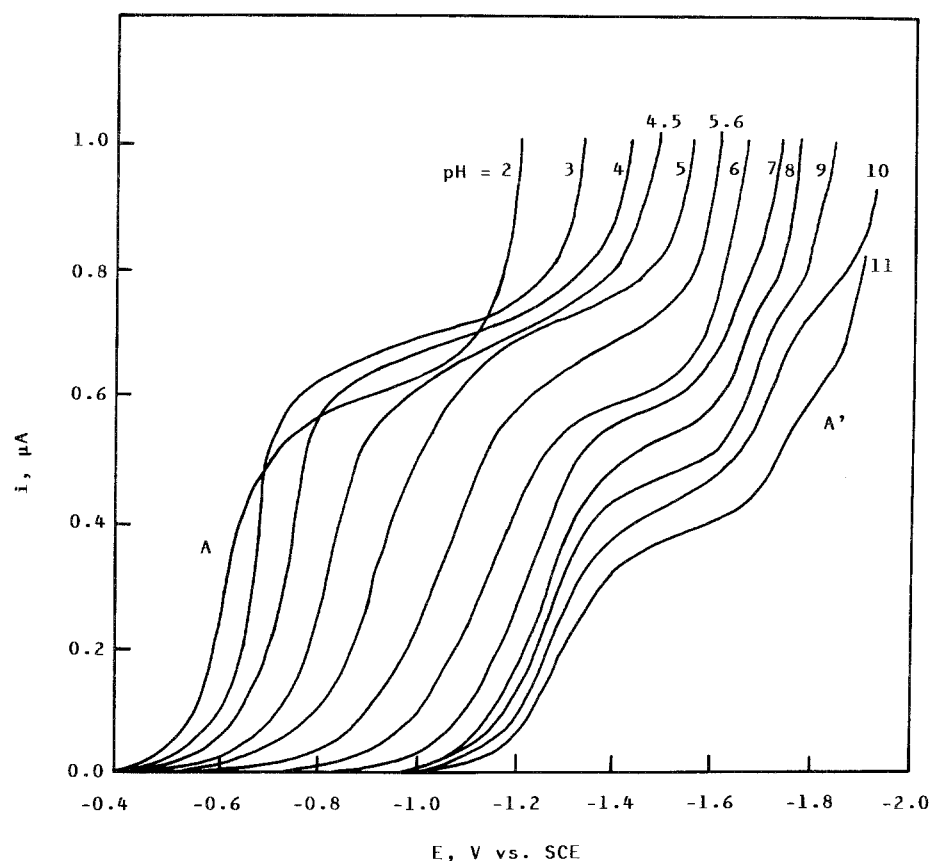


Fig. 1. DC-polarograms of $2.22 \times 10^{-4} M$ of TCGA in 20% (v/v) ethanolic Britton-Robinson buffer solutions at 298.15 K

Table 3. DC-polarographic data obtained for $2.22 \times 10^{-4} M$ TCGA in solutions of different pH values at 298.15 K (wave A) ($S_1 = 0.0591/\alpha n_a$, $S_2 = \Delta E_{1/2}/\Delta pH$)

pH	$-E_{1/2}$ (Ag/AgCl)	S_1 (mV)	$D^\circ \times 10^{-6}$ cm ² /sec	S_2 (mV)	αn_a	$K_{f,h}^\circ$ cm ⁻¹	ΔG^* kJ/mol
2.0	0.60	117	4.54	90.9	0.78	4.33×10^{-9}	325.14
3.0	0.67	117	4.86	86.4	0.73	1.38×10^{-9}	337.14
4.0	0.74	117	4.60	90.9	0.74	5.70×10^{-10}	346.42
5.0	0.94	195	5.89	125.0	0.43	8.60×10^{-10}	342.10
6.0	1.13	195	3.33	125.0	0.42	7.01×10^{-11}	368.40
7.0	1.22	15	3.10	105.0	0.56	4.67×10^{-14}	445.13
8.0	1.24	15	2.39	77.6	0.76	3.24×10^{-18}	545.58
10.0	1.27	15	2.02	74.6	0.85	7.42×10^{-19}	561.10
11.0	1.28	15	4.54	67.9	0.63	1.67×10^{-20}	600.85

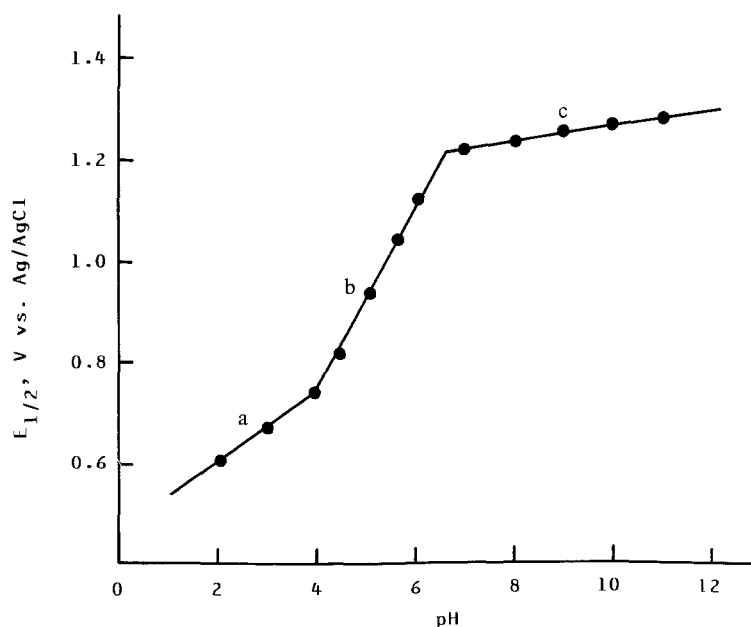


Fig. 2. $E_{1/2}$ - pH plot of the polarographic waves of $2.22 \times 10^{-4} M$ of TCGA in 20% (v/v) ethanolic Britton-Robinson buffers at 298.15 K

pH (Fig. 2) a broken line consisting of three segments a, b and c is obtained and the breaks occurred at pH about 4 and 7. The slopes (S_1) of the segments are 50, 200 and 23 mV/ pH , respectively. The breaks occurred at pH values corresponding to the pK_1^H and pK_2^H which are in good agreement with those obtained from potentiometric measurements (Table 1).

Analysis of the polarographic wave of TCGA at different pH values was performed using the equation due to Meites [21]. On plotting $E_{d,e}$ versus $\log(i/i_a - i)$, straight lines were obtained with slopes (S_2) represented in Table 3. These slopes were utilized in the evaluation of αn_a values in which α is the transfer coefficient and n_a is the number of electrons involved in the rate-determining step (r.d.s). The calculated values of α -parameter (Table 3) revealed that the reduction process proceeds irreversibly in all solutions, since values of α are less than 0.7 at $n_a = 1.0$. Also, from the slopes S_1 and S_2 , the number of the hydrogen ions (Z_H^+) participating in the r.d.s. was calculated [20]. The results revealed that in solutions of $4 > pH > 7$, Z_H^+ equals to unity, i.e. the rate-determining step in this range of pH involves one electron and one proton.

Cyclic Voltammetry

The voltammograms of TCGA were investigated in solutions of pH 3.4. and 8.5. The voltammograms at different scan rate (20–500 mV/s) in solution of pH 3.4 exhibited a single cathodic peak, whereas in solution of pH 8.5, two distinct cathodic peaks were observed (Fig. 3). The absence of any peaks in the reverse scan as well as the shift of peak potential (E_p) to more negative values on increasing the scan rate (v) revealed the irreversible nature of the reduction waves as indicated

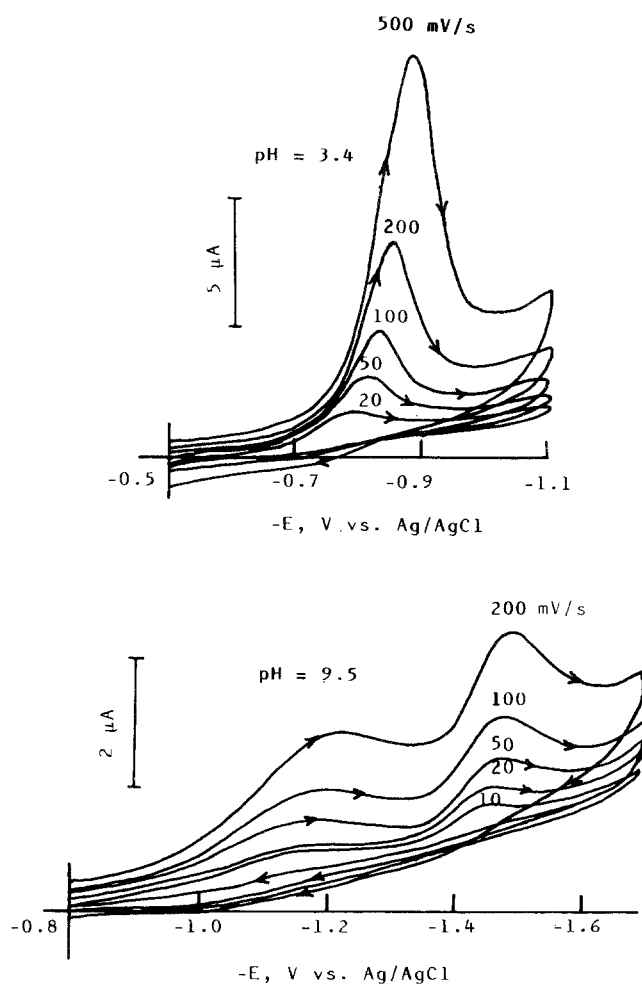


Fig. 3. Cyclic voltammograms of TCGA using different scan rates at 298.15 K

before from dc-polarography. Furthermore, the irreversibility was ascertained by evaluating the transfer coefficient (α) using equation [22]:

$$E_p = -1.14 \frac{RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{K_{f,h}}{D^{1/2}} - \frac{RT}{\alpha n_a F} \ln(\alpha n_a v).$$

On plotting E_p versus $\ln v$ at different pH values, straight lines of slopes equal to $0.0128/\alpha n_a$ were obtained. The αn_a values were calculated and found to be 0.44 at pH 3.4 and amounting to 0.49 and 0.77 for the first and second peaks, respectively, at pH 8.5. These values of α -parameter were found to be in good agreement with those obtained from dc-polarography (Table 3).

According to Delahy [23] for the irreversible electron-transfer process, i_p is correlated to the scan rate v by equation [24],

$$i_p = 3.01 \cdot 10^5 n(\alpha n_a) A D^{1/2} C^0 v^{1/2},$$

where i_p is the peak current in amperes, and the remaining terms have the usual significance. The linear correlations of i_p versus $v^{1/2}$ passing through the origin in solutions of pH 3.4 and 8.5 revealed that the reduction process is mainly controlled by diffusion [24].

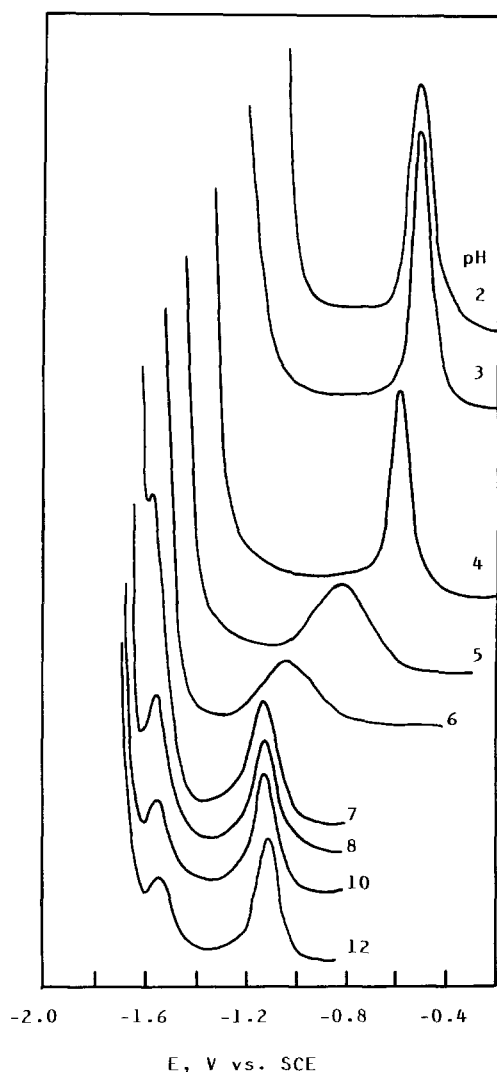


Fig. 4. DP-polarograms of *TCGA* in 20% (v/v) ethanolic Britton-Robinson buffer solutions at 298.15 K

Differential Pulse Polarography

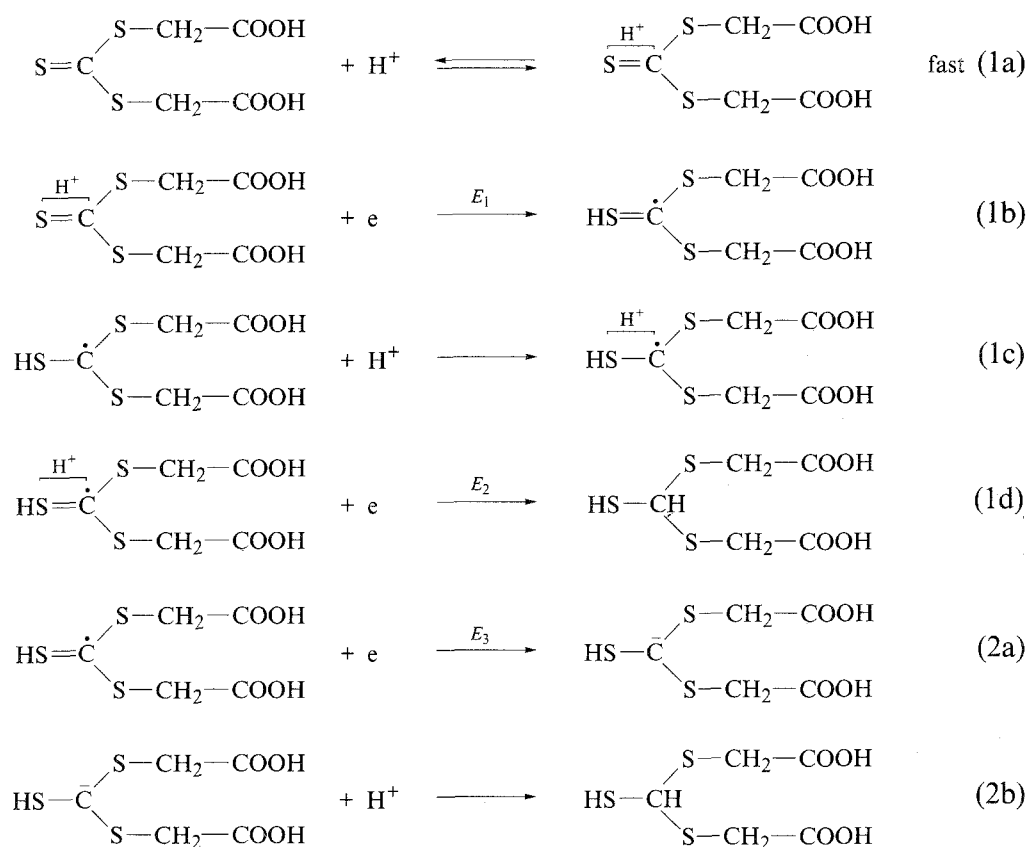
Differential pulse (dp) polarography is used as a tool for characterising electrode processes due to its advantage over the dc-polarography in sensitivity, rapidity and elimination of charge effects. The differential pulse parameters of *TCGA* (E_p , $W^{1/2}$) are *pH*-dependent, indicating that hydrogen ions are involved in the electrochemical process. Figure 4 shows the dp-polarograms of *TCGA* at different *pH* values. The dp-polarograms exhibited a single peak in solution of *pH* < 7, whereas at *pH* > 7 two peaks are obtained. The peak potential (E_p) is shifted to more negative values on increasing the *pH*. The half peak width ($W^{1/2}$) equals to 90 mV, denoting the irreversible nature of the electrode process. For a reversible 2-electron transfer $W^{1/2}$ should equal to 45 mV at a pulse amplitude 25 mV [25].

Controlled Potential Coulometry (CPC)

Controlled potential coulometry was performed to determine the number of electrons (*n*) consumed in the reduction process using a large mercury pool cathode

whose potential was maintained at a value corresponding to the limiting current of the polarographic wave using a potentiostat. The measurements were carried out in acidic and alkaline solutions. The electrolysis cell was a 150 ml beaker in which the reference electrode (SCE), auxiliary electrode (platinum wire) and the gas inlet were introduced by means of a cork. The progress of electrolysis was followed by recording the decrease in current with time and the number of electrons (n) was computed from $i-t$ curves following the procedure outlined by Lingan [26] and found to be $2e \pm 0.2$ in both acidic and alkaline solutions.

From cpc measurements, it was found that 2 electrons/molecule are involved in the reduction process in both acidic and alkaline solutions. The C=S is only the electroactive center within the depolarizer molecule. So on the basis of the data given from dc-, dp-polarography and cyclic voltammetry, the following reaction pathway is proposed:



In acidic media, the equilibrium (c) is so rapidly established that all the depolarizer is reduced along the path described by equations (1a), (1b), (1c) and (1d) in which $E_1 \approx E_2$. This gives one 2-electron wave, because the potential E_2 is not sufficiently more negative than E_1 . As the pH increases, the rate of protonation of the radical (equation 1c) decreases, until finally the reduction follows the path described by equations (1a), (1b), (1c), (2a) and (2b), in which E_3 is sufficiently more negative than E_1 and the polarograms in alkaline solutions show two 1-electron

waves [20], i.e. in acid solution the mechanism of the electrode process is H^+ , e, H^+ , e, whereas in alkaline ones is H^+ , e, e, H^+ .

Kinetic Parameters

The kinetic parameters of the electrode reaction were calculated from dc-polarography using the equations of Koutecky [27] and Heyrovsky [28]. Table 3 includes representative values for the heterogeneous rate constant ($K_{f,h}^0$) and free energy of activation (ΔG^*). The data given in Table 3 revealed that ($K_{f,h}^0$) decreases on increasing the *pH* of the solution, denoting that the electron-transfer process becomes slower at higher *pH*. Also, the values of ΔG^* generally increase with increasing the *pH* revealing that the reduction process becomes more difficult at higher *pH* values.

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