

Electrochemical oxidation of thiocyanate in a two-phase electrolyte

P. KRISHNAN, V. G. GURJAR*

Department of Chemical Engineering, Indian Institute of Technology, Bombay-400 076, India

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A two phase electrolysis method has been developed for preparation of thiocyanating reagent. The electrolyses were carried out using graphite electrodes using a two phase electrolytic medium made up of an aqueous solution of ammonium thiocyanate in 0.25 M H₂SO₄ and a nonaqueous solvent. The effect of experimental parameters, such as temperature and duration of electrolysis, nature of the nonaqueous solvent and volume fraction of the nonaqueous phase, on the process current efficiency were studied. The voltammetric studies in the nonaqueous phase established that trithiocyanate, (SCN)₃⁻¹, was produced in the aqueous phase and was subsequently extracted into the nonaqueous phase.

1. Introduction

Thiocyano derivatives of organic compounds find applications as agrochemicals, dye and drug intermediates and serve as precursors in the preparation of nitrogen and sulphur containing heterocycles [1, 2]. The pseudo halogen, thiocyanogen, (SCN)₂, is mainly employed for the preparation of thiocyanate derivatives of organic compounds. Thiocyanogen is usually prepared by the oxidation of thiocyanates using oxidizing agents like chlorine and bromine in nonaqueous solvents. The handling of such hazardous oxidizing agents and the simultaneous formation of halo substituted derivatives are the main disadvantages of this method. The above disadvantages can be overcome in electrochemical thiocyanation and an interesting two phase electrochemical method for thiocyanation of organic compounds has been reported [3, 4].

Investigations carried out to determine the optimum experimental conditions for the electrochemical preparation of the thiocyanating reagent and to establish its identity are discussed in this communication.

2. Experimental details

All the chemicals used were of analytical grade. The dichloromethane was purified according to the reported purification method [5]. The aqueous solutions were prepared with double distilled water. The experiments at low temperature were carried out by placing the cell in a bath through which ethylene glycol was circulated from a cryostat.

2.1. Preparatory scale study

Preparative scale experiments were carried out in an

undivided cylindrical cell of capacity 300 ml. Three rectangular graphite plate electrodes (geometrical area 20 cm² each), one anode and two cathodes, placed at an interelectrode distance of 3 mm were used for the electrolysis. The electrolytic medium contained 65 ml aqueous solution of 2 M NH₄SCN in 0.25 M H₂SO₄, and 65 ml of nonaqueous solvent. The cell contents were thoroughly mixed by a magnetic stirrer.

After completion of the electrolysis, the two phases were separated and analysed for the thiocyanating reagent by the iodometric method and the process current efficiency was determined.

2.2. Voltammetric studies

A single compartment jacketed cell built around a 29/32 GG joint was used. A platinum microelectrode of geometrical area 0.008 cm² was used as the working electrode. All measurements were carried out at 0°C. Other experimental details are the same as reported earlier [4].

3. Results and discussion

Electrolysis of aqueous solutions of ammonium thiocyanate was carried out with and without hydrochloric, sulphuric and perchloric acids. The current efficiency for formation of the thiocyanating reagent was about 10% due to the unstable nature of the product in aqueous solutions.

Since the thiocyanating reagent readily decomposed in aqueous solutions, it was decided to carry out the electrolysis in a mixed electrolyte containing both aqueous and nonaqueous phases. The decomposition of thiocyanating reagent was suppressed in

* To whom correspondence should be addressed.

Table 1. Effect of the nature of the nonaqueous solvent on current efficiency

Current density: 15 mA cm^{-2} ; concentration of ammonium thiocyanate*: 1.0 M ; quantity of electricity: 0.15 Ah ; electrolysis temperature: 0°C

No.	Nonaqueous solvent	(SCN) ₂ in aqueous phase /mM	(SCN) ₂ in nonaq. phase /mM	Current efficiency* /%
1	—	0.95	—	34.2
2	CCl ₄	0.88	—	33.2
3	CHCl ₃	0.55	0.85	50.0
4	C ₂ H ₄ Cl ₂	0.30	1.75	73.5
5	CH ₂ Cl ₂	0.30	1.64	69.2

* Calculated with respect to the total electrolyte volume

the two phase medium due to its extraction into the nonaqueous solvent.

The results of two phase electrolysis with various nonaqueous solvents are presented in Table 1. It can be seen that the thiocyanating reagent is not extractable into carbon tetrachloride and chloroform. However, it is readily extracted into dichloromethane and dichloroethane and these two solvents have therefore been found suitable for two phase electrolysis.

To study the effect of electrolysis temperature on the stability of thiocyanating reagent, electrolyses were carried out at various temperatures. The current efficiency values obtained are presented in Fig. 1. It is evident that the stability of the thiocyanating reagent is affected by the temperature of electrolysis. At higher temperatures (more than 2°C) it was polymerized to an insoluble yellowish powder. However, the polymerization could be completely avoided at lower temperatures, for example, at 0°C . Therefore all further experiments were carried out at this temperature.

The current efficiencies obtained for various durations of electrolysis are given in Fig. 2. It can be seen that the current efficiency drops with increase in electrolysis duration. This is because as soon as the saturation concentration of the thiocyanating reagent in the nonaqueous solvent is reached, further

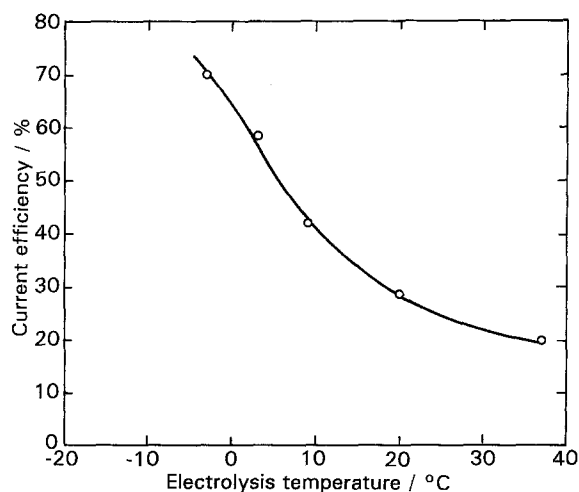


Fig. 1. The effect of electrolysis temperature on the current efficiency. Electrolyte: 65 ml of $2 \text{ M NH}_4\text{SCN}$ in $0.25 \text{ M H}_2\text{SO}_4$ + 65 ml of dichloromethane; current density: 15 mA cm^{-2} ; duration of electrolysis; 30 min.

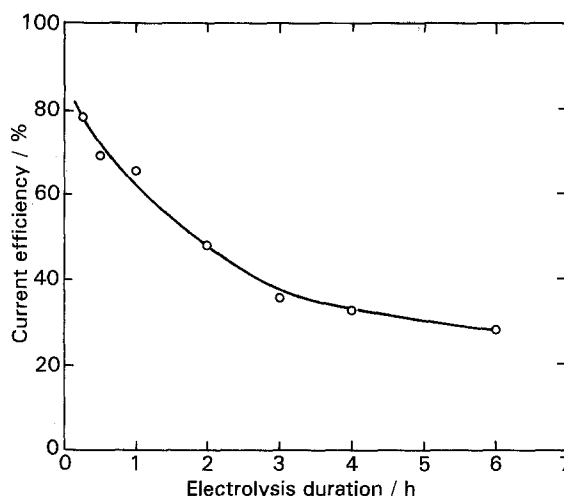


Fig. 2. Variation of current efficiency with the electrolysis duration. Electrolyte: 65 ml of $2 \text{ M NH}_4\text{SCN}$ in $0.25 \text{ M H}_2\text{SO}_4$ + 65 ml of dichloromethane; current density: 15 mA cm^{-2} ; temperature: 0°C .

extraction almost stops and the thiocyanating reagent remaining in the aqueous phase is decomposed.

The current efficiency obtained for various volume fractions of the organic to the aqueous phase are plotted in Fig. 3. Under the electrolysis conditions, the current efficiency for formation of the thiocyanating reagent increases with increase in the volume fraction of the organic phase. This further supports the above observation that the thiocyanating reagent has a limited solubility in the nonaqueous phase. However, it was not possible to employ an organic phase volume fraction of more than 0.5 since the passage of electricity through the medium becomes difficult and unsteady at higher organic phase volume fractions.

The current efficiency is mainly affected by the concentration of thiocyanate in the aqueous solution. A high concentration of thiocyanate ($<1.0 \text{ M}$) is necessary to obtain a current efficiency of around 75%. The current efficiency is also affected by the current density employed for the electrolysis. The effect of these parameters have also been studied and the

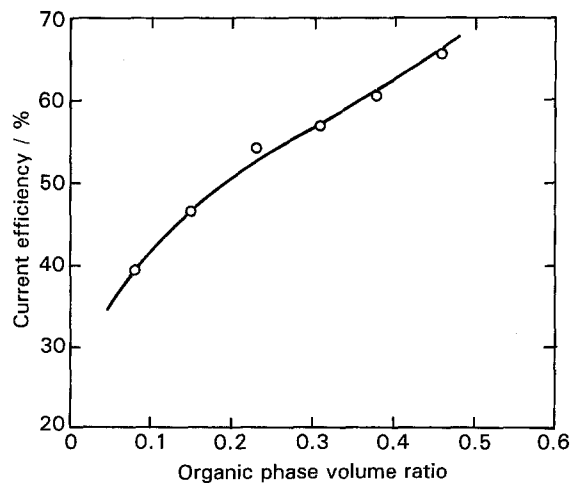


Fig. 3. The effect of organic to the aqueous phase volume ratio on the current efficiency; total electrolyte volume: 130 ml; aqueous phase: $2 \text{ M NH}_4\text{SCN}$ in $0.25 \text{ M H}_2\text{SO}_4$; nonaqueous solvent: dichloromethane; current density: 15 mA cm^{-2} ; duration of electrolysis: 30 min.

Table 2. Desired values of experimental parameters for the electrochemical preparation of thiocyanogen by two phase electrolysis

No.	Experimental condition	Desired value
1	Current density	15 mA cm ⁻²
2	Electrolysis duration	3 h
3	Aqueous-nonaqueous volume ratio	50 : 50
4	Concentration of thiocyanate	1–2 M
5	Electrolysis temperature	0°C

most favourable experimental conditions for the preparation of the thiocyanating reagent are given in Table 2.

3.1. Voltammetric studies in the nonaqueous solvents

After determining the best experimental conditions for electrochemical preparation of the thiocyanating reagent by two phase electrolysis, further experiments were carried out to establish the identity of the thiocyanating reagent. It has been reported that trithiocyanate is the species produced during the electrochemical oxidation of thiocyanate in the acidic medium [6]. However, Arvia *et al.* [7, 8] have reported thiocyanogen as the thiocyanating species produced during electrochemical oxidation in nonaqueous solvents. Therefore, it was felt necessary to carry out voltammetric studies in the solution of thiocyanating reagent in the nonaqueous phase in order to identify the species produced during the two phase electrolysis. The nonaqueous solvent, dichloromethane, was thoroughly mixed for 2 h with an equal volume of 2.0 M aqueous solution of ammonium thiocyanate. It

was then separated from the aqueous solution and dried over anhydrous sodium sulphate. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP, 0.10 M) was added to make it conducting and voltammograms were recorded within the potential range 0.0–1.50 V vs SCE using a platinum micro electrode. The absence of a voltammetric peak corresponding to the oxidation of thiocyanate in the potential region 0.50–1.20 V shows that ammonium thiocyanate is virtually insoluble in dichloromethane.

Two phase electrolysis was carried out for 2 h under the experimental conditions given in Table 2. The organic phase was separated from the aqueous phase and dried over anhydrous sodium sulphate. Then the supporting electrolyte (TBAP 0.10 M) was added and voltammograms were recorded in this solution. A typical voltammogram is shown in Fig. 4. The forward potential sweep was initiated at 0.40 V, and the electrode potential was then scanned between 1.50 and –1.00 V. The potential sweep was terminated at 0.40 V. No oxidation wave was observed during the first forward sweep showing that the thiocyanating species extracted into the nonaqueous solvent does not undergo further oxidation at the electrode. During the return sweep, reduction of thiocyanating reagent begins at 0.30 V and a broad peak (II_c) is obtained around –0.30 V. However, from the second cycle onwards, an oxidation wave (I_a) appears during the forward sweep which gives the corresponding reduction wave (I_c) during the reverse sweep.

Peaks (I_a) and (I_c) are irreversible as their potentials are separated by around 0.20 V and the difference increases with increase in the sweep rate. At sweep

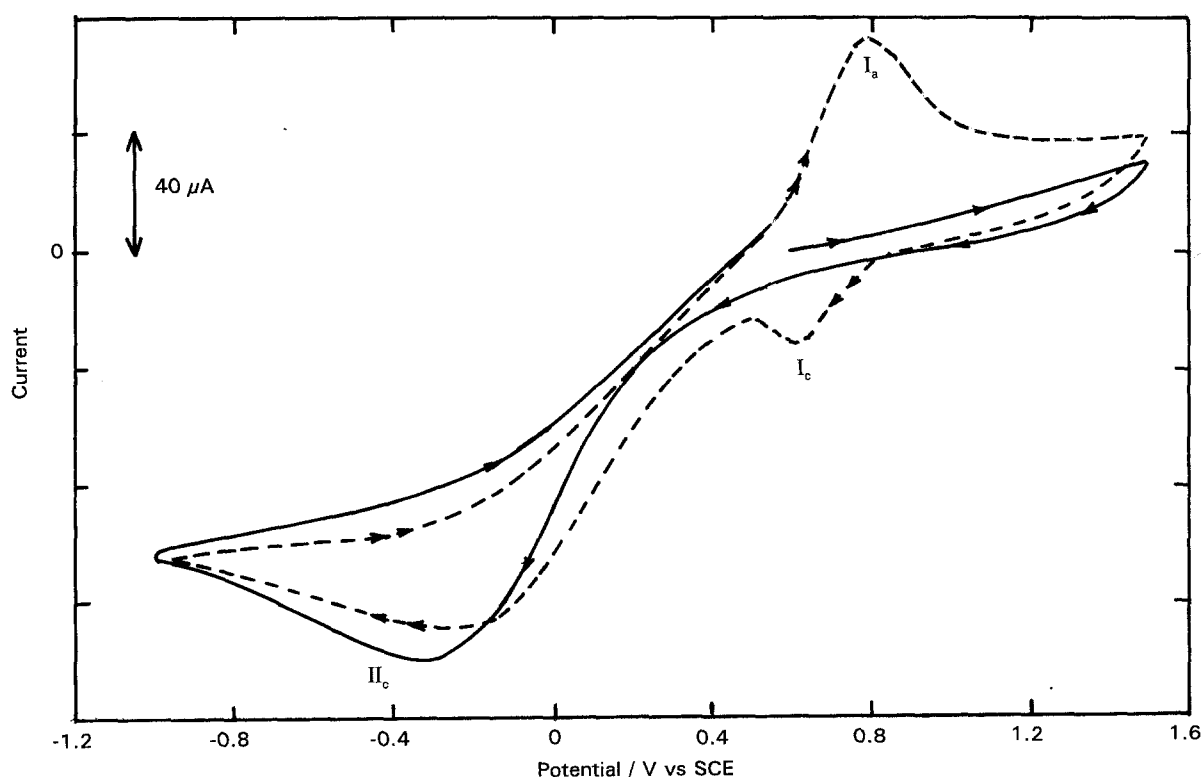


Fig. 4. Cyclic voltammograms recorded in the solution of the thiocyanating reagent in dichloromethane. Sweep rate: 0.20 V s⁻¹; temperature: 0°C. (—) First cycle; (---) second cycle.

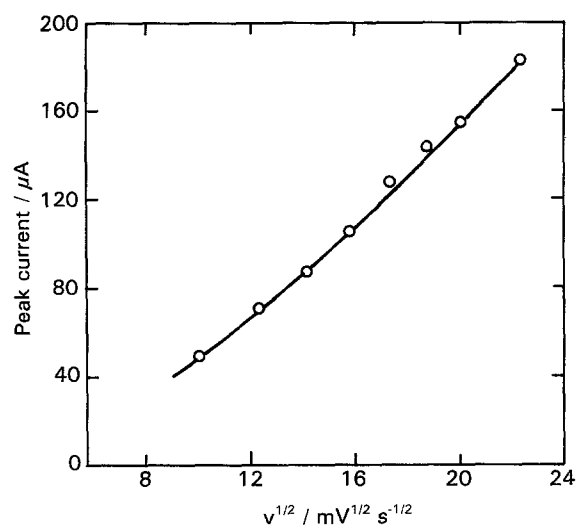


Fig. 5. Peak current (i_p) against square root of sweep rate (v)^{1/2} plot for the oxidation wave (I_a).

rates higher than 0.5 V s^{-1} the reduction wave (I_c) merges with that for the reduction of thiocyanating reagent (II_c).

The magnitude of both anodic and cathodic peak currents ($i_p(I_a)$, $i_p(I_c)$) increase with sweep rate as well as the number of cycles. The peak current for the oxidation wave ($i_p(I_a)$) was plotted against the square root of sweep rate (Fig. 5). A straight line passing through the origin indicates that the oxidation wave (I_a) is diffusion controlled.

The appearance of the oxidation wave (I_a) only from the second cycle onwards indicates that this wave is due to oxidation of the species produced during the reduction of the thiocyanating reagent. This is further supported by the fact that the oxidation wave

(I_a) is observed during the first cycle itself if the forward potential sweep is initiated at -1.0 V instead of 0.40 V . In the latter case, the thiocyanating reagent is reduced at the electrode during the forward sweep until the electrode potential reaches 0.30 V . The species produced during this reduction process undergoes oxidation at potentials above 0.50 V .

Since thiocyanate has been reported as the product of the electrochemical reduction of both trithiocyanate and thiocyanogen [4, 5], it can be assumed that the oxidation wave (I_a) is due to the oxidation of thiocyanate produced during the reduction of the thiocyanating reagent. To confirm this, voltammograms were recorded in a solution of 0.5 mM tetrabutylammonium thiocyanate in dichloromethane. A typical voltammogram is given in Fig. 6. The figure shows that only one oxidation–reduction couple is observed within the potential range 0.0 to 1.60 V . This couple is virtually identical to the I_a/I_c couple observed in Fig. 4. Observation of the reduction wave (I_c), different from that for reduction of the thiocyanating reagent (II_c), shows that the species formed during the electrochemical oxidation of thiocyanate in the nonaqueous solvents is distinctly different from that formed in the aqueous phase and extracted into the nonaqueous phase during the two phase electrolysis. Since the species formed in the aqueous acidic solutions has been identified as trithiocyanate [6], it may be concluded that trithiocyanate is the species extracted into the nonaqueous solvent during two phase electrolysis and thiocyanogen is the thiocyanating species produced during the electrochemical oxidation of thiocyanate in the nonaqueous solvents.

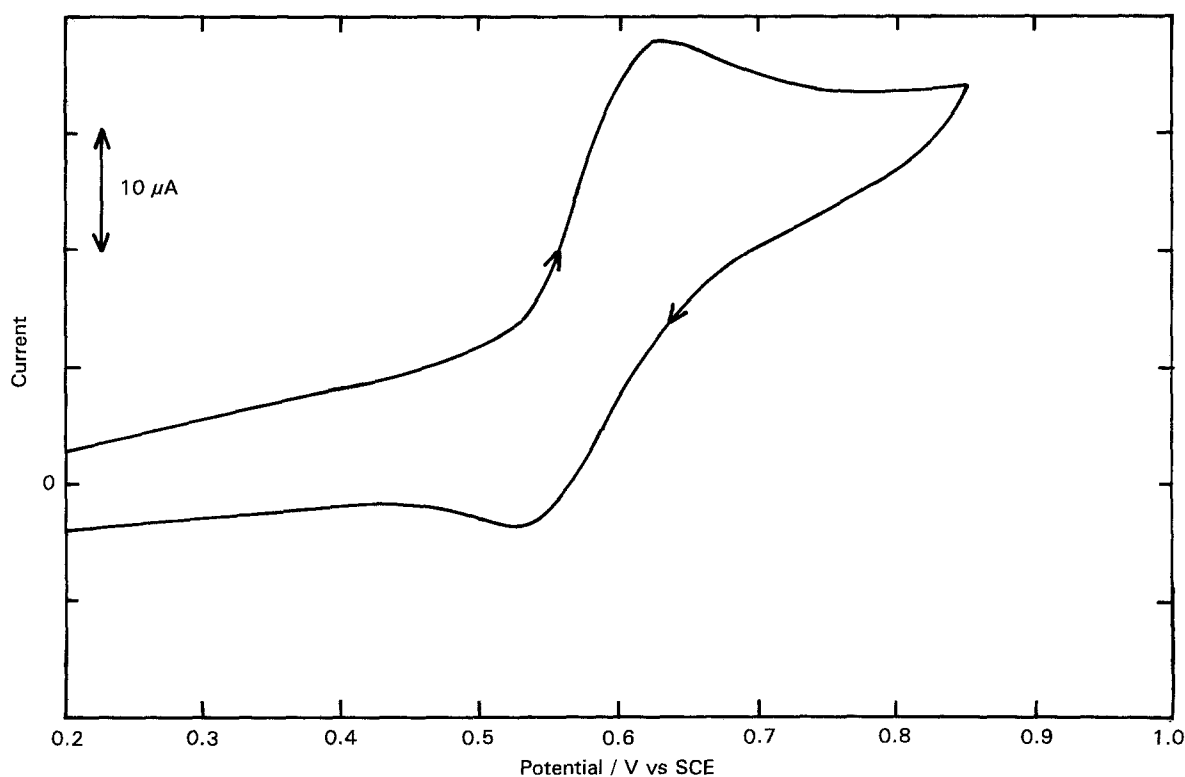


Fig. 6. Cyclic voltammogram for the 0.001 M tetrabutylammonium thiocyanate in dichloromethane. Sweep rate: 0.100 V s^{-1} ; temperature: 0°C .

4. Conclusion

Electrolysis of aqueous acidic ammonium thiocyanate solutions yielded a current efficiency around 10%. The low current efficiency values were due to chemical decomposition of the thiocyanating reagent in the aqueous electrolyte. It is possible to obtain 70% current efficiency by employing two phase electrolysis. The current efficiency is affected by experimental factors like the nature of the nonaqueous solvent, the temperature of electrolysis, the duration of electrolysis, the volume fraction of the aqueous to nonaqueous phases, the concentration of thiocyanate and the current density.

Trithiocyanate is the stable species produced in the acidic solutions and is extracted into the nonaqueous solvent during two phase electrolysis, whereas, thiocyanogen is the thiocyanating reagent produced

during the electrochemical oxidation of thiocyanate in the nonaqueous solvents.

References

- [1] D. L. Mackinnon and A. P. Farrell, *Environ. Toxicol. Chem.* **11** (1992) 1541.
- [2] R. G. Guy, in 'The chemistry of cyanates and their thio derivatives - Part 2, (edited by S. Patai), John Wiley & Sons, Chichester (1977) Chap. 18.
- [3] P. Krishnan and V. G. Gurjar, *Syn. Commun.* **22** (1992) 2741.
- [4] *Idem*, *J. Appl. Electrochem.* **23** (1993) 268.
- [5] D. D. Perrin, W. L. F. Armarego and D. R. Perrin (Eds), 'Purification of laboratory chemicals' Pergamon, Oxford (1966).
- [6] E. Itabashi, *J. Electroanal. Chem.* **177** (1984) 311.
- [7] R. Pereiro, A. J. Arvia and A. J. Calandra, *Electrochim. Acta* **17** (1972) 1723.
- [8] C. Martinez, A. J. Calandra and A. J. Arvia, *ibid.* **17** (1972) 2153.