Determination of the Second Ionization Constant of 3,5-Dinitrosalicylic Acid (DNSH$_2$) and the Instability Constant of [DNSFe]$^+$ and Titrimetric Determination of Thiourea with a 3,5-Dinitrosalicylate-Selective Electrode

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Measurements made with a combination of glass and 3,5-dinitrosalicylate-selective membrane electrode in DNSHNa solutions varying in pH and ionic strength have been used to determine the second ionization constant of 3,5-dinitrosalicylic acid. Also the instability constant of the complex [DNSFe]$^+$ has been determined by titrating known amounts of iron(III) with standard DNSHNa solution. A method has been developed for the semiautomatic potentiometric titration of thiourea with silver nitrate in the presence of 3,5-dinitrosalicylate ions, using the aforementioned selective electrode. Thiourea in the range 1.5–15 mg was determined with average relative error and relative standard deviation of about 1%. © 1986 Academic Press, Inc.

INTRODUCTION

Ion-selective electrodes have been used for the potentiometric determination of equilibrium constants by ion-activity measurements (5–7). Recently, we reported a new 3,5-dinitrosalicylate (DNS)-selective membrane electrode and its application to the potentiometric determination of various substances (4).

In this paper, the potentiometric determination of the second ionization constant of 3,5-dinitrosalicylic acid and of the instability constant of the [DNSFe]$^+$ complex is described. The values obtained for the pK_{a_2} and the instability constant of [DNSFe]$^+$ (pH 2.5) at 25°C and zero ionic strength are 7.25 and 10.57, respectively, in close agreement with reported values (8, 9). A titrimetric method for the determination of thiourea in the presence of sodium 3,5-dinitrosalicylate (DNSHNa) is also described. The method is based on the formation of isoluble complexes of silver thiourea–dinitrosalicylate, [Ag(SCN$_2$H$_4$)$_2$] (DNSH) or [Ag(CSN$_2$H$_4$)] (DNSH). Thiourea in the range 20–200 μmol was determined in a sample volume of 20 ml with relative errors of about 1%.

Theory of Measurements

(a) *Determination of the* pK_{a_2} *of 3,5-dinitrosalicylic acid.* The response of the electrode is given by

$$E = E' - S \log[\text{DNSH}^-] \tag{1}$$

where S is the experimentally determined slope of the electrode. From the re-

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ported values of ionization constants of $DNSH_2$ ($pK_{a_1} = 0.70$, $pK_{a_2} = 7.25$) (*I*, *8*) it is concluded that in the pH range 2–6 the predominant species in solution is the $DNSH^-$ ion. In this range $[DNSH^-] \simeq C$, where C is the analytical concentration of $DNSH_2$. The potential of the electrode is practically independent of pH and equal to

$$E_0 = E' - S \log C. \tag{2}$$

For pH > 6 we have

$$a_1 = \frac{[DNSH^-]}{C} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \simeq \frac{[H^+]}{[H^+] + K_2}. \tag{3}$$

Combining Eqs. (1), (2), and (3),

$$E-E_0 = S \log \left(\frac{K_2}{[H^+]} + 1 \right) \tag{4}$$

and with rearrangement

$$-\log [10^{(E - E_0)/S} - 1] = pK_{a_2} - pH. \tag{5}$$

From Eq. (5) it is clear that plots of the left factor of the equation vs pH should yield a linear relationship of slope -1 with intercept pK_{a_2}.

(*b*) *Determination of the instability constant of the [DNSFe]$^+$ complex.* $DNSH_2$ is known to give a characteristic color reaction with iron(III). Vassiliadis *et al.* (9) have shown that $DNSH_2$ forms only one complex with iron(III) (1:1), [DNSFe]$^+$, and proposed the form
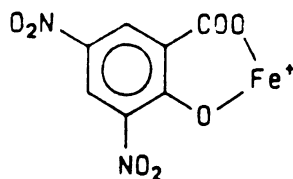
For the dissociation of the complex

$$[DNSFe]^+ \leftrightarrows DNS^{2-} + Fe^{3+}$$

we have

$$K_{inst} = \frac{[DNS^{2-}][Fe^{3+}]}{[DNSFe^+]} \tag{6}$$

or taking in'o consideration the second dissociation of $DNSH_2$,

$$K_{inst} = \frac{K_2[DNSH^-][Fe^{3+}]}{[H^+][DNSFe^+]}. \tag{7}$$

If C_{Fe} and C_{DNSH_2} represent the analytical concentration of iron and 3,5-dinitros-alicylate, in the pH range 3–5 it is $C_{DNSH^-} \simeq C_{DNSH_2}$. Therefore, we have

$$[DNSFe^+] = C_{DNSH^-} - [DNSH^-] \tag{8}$$

$$[Fe^{3+}] = C_{Fe} - [DNSFe^+] = C_{Fe} - C_{DNSH^-} + [DNSH^-]. \tag{9}$$
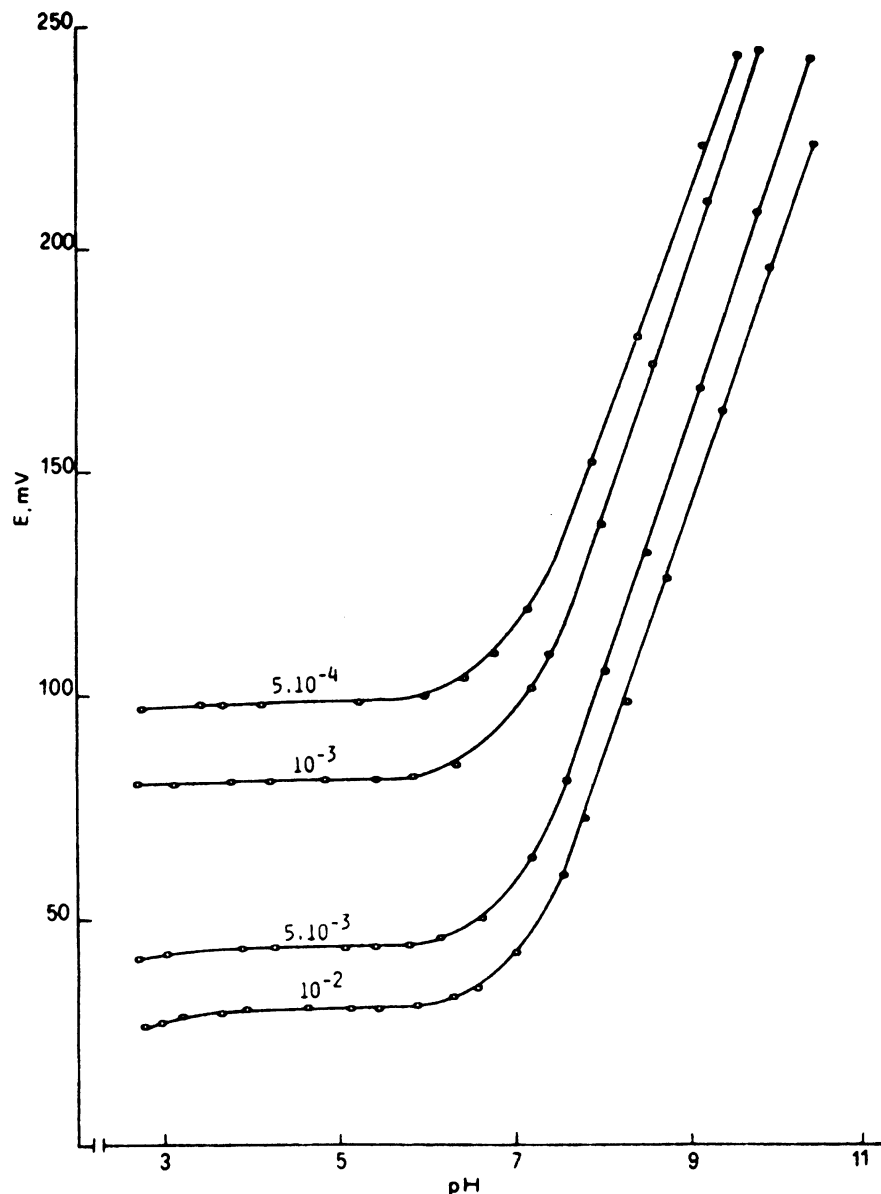
FIG. 1. Effect of pH on the potential of the 3,5-dinitrosalicylate-selective electrode at the different concentrations of monosodium 3,5-dinitrosalicylate marked at constant ionic strength $\mu = 0.2\ M$.

Combining Eqs. (7)–(9),

$$K_{inst} = \frac{K_2[DNSH^-]}{[H^+]} \cdot \frac{(C_{Fe} - C_{DNSH^-} + [DNSH^-])}{C_{DNSH^-} - [DNSH^-]}. \tag{10}$$

From Eq. (10) the K_{inst} of the complex $[DNSFe]^+$ can be calculated. $[DNSH^-]$ values are calculated from potential measurements with the DNS-selective electrode.

MATERIALS AND METHODS

Reagents

All solutions were prepared with distilled deionized water from reagent-grade materials.

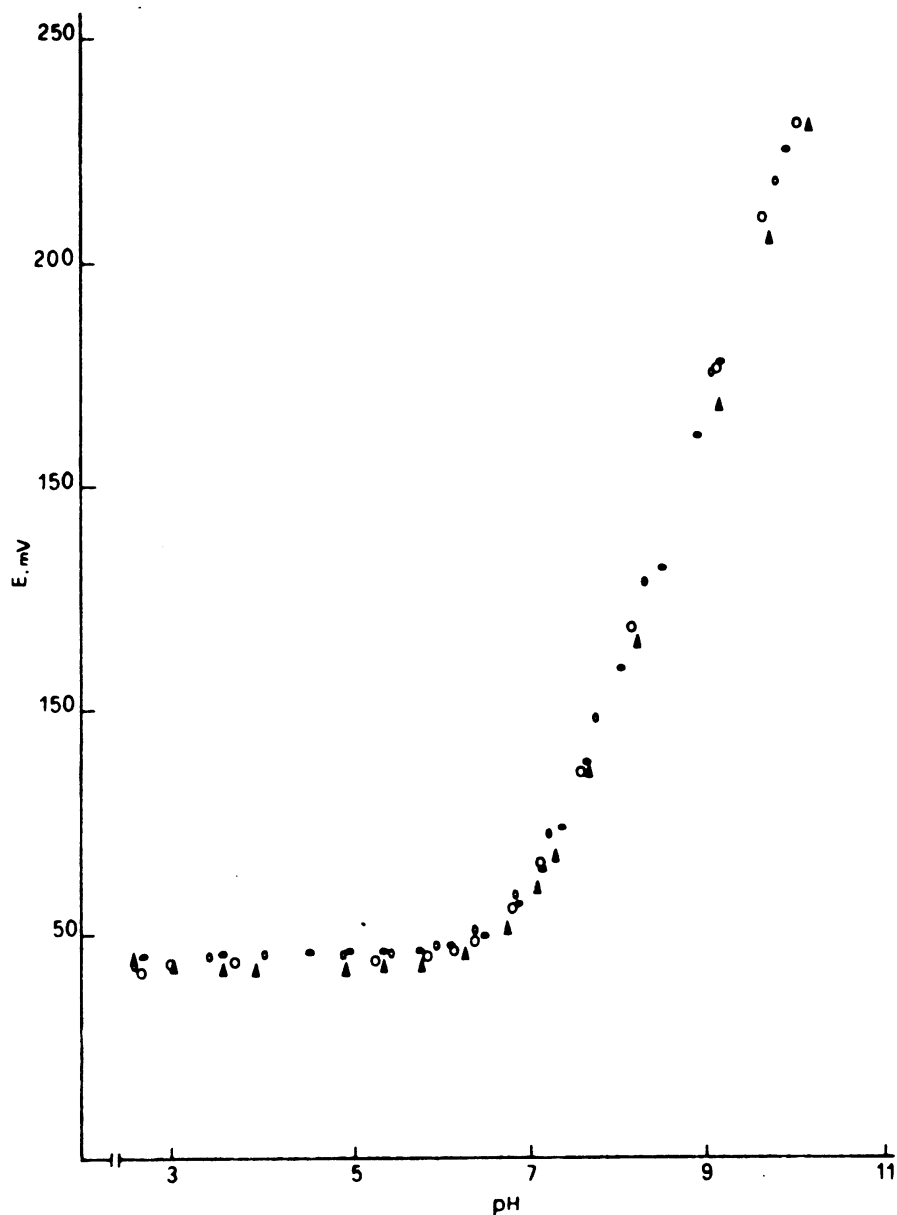Monosodium 3,5-dinitrosalicylate (DNSHNa) solution, 0.01000 /l, was pre-

FIG. 2. Effect of pH on the potential of the 3,5-dinitrosalicylate-selective electrode at different ionic strength values μ = 0.1 M (▲); 0.2 M (●); 0.4 M (○); 1.0 M (O). [DNSHNa] = 5.00 × 10^{-3} M.

pared by dissolving 2.680 g of DNSHNa (Eastman Kodak) in water and diluting to 1 liter.

Iron(III) solution, 0.0100 M, was prepared by dissolving 4.822 g of $Fe(NH_4)$ $(SO_4)_2 \cdot 12H_2O$ in 2% sulfuric acid solution and diluting to 1 liter with the same solution.

Thiourea solution, 0.01000 M, was prepared by dissolving 0.7612 g of thiourea (Merck, 99.5%) in water and diluting to 1 liter.

Silver nitrate solution, 0.01000 M, was prepared by dissolving 0.8494 g of silver nitrate in water and diluting to 500 ml.

Apparatus

The DNS-selective electrode was constructed, used, and stored as previously described (4), in conjuction with an Orion 90-01 Ag–AgCl single junction reference electrode. The cell potential was recorded with a Heath–Schlumberger
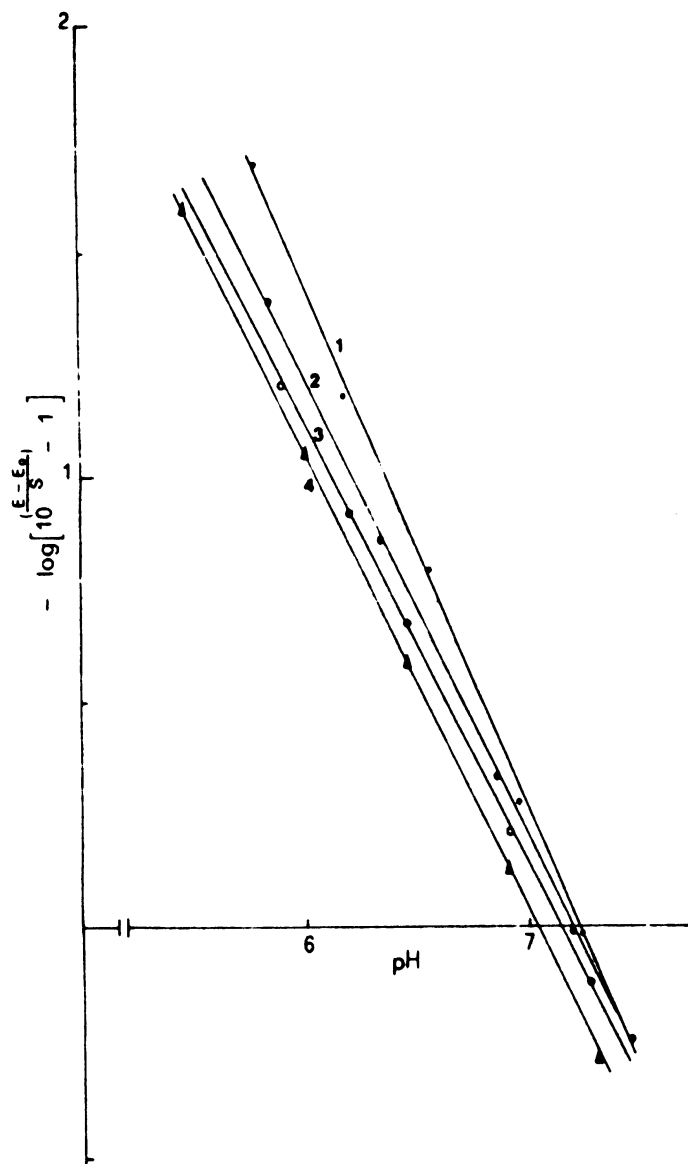
FIG. 3. Evaluation of pK_{a_2} at various ionic strengths: (1) 0.1 M; (2) 0.2 M; (3) 0.4 M; and (4) 1.0 M. [DNSHNa] = 5.00 × $10^{-3} M$.

system (*3*). pH values were measured with a combination glass elec rode and a Corning Model 12 mV/pH meter. Measurements were carried out i ito a 50-ml double-walled glass cell, at 25.00 ± 0.2°C, with effective magnetic stirring.

Procedures

Determination of DNS-electrode slope at various ionic strength values. Elec-

TABLE 1

Values of pK_{a_2} at Various Ionic Strengths

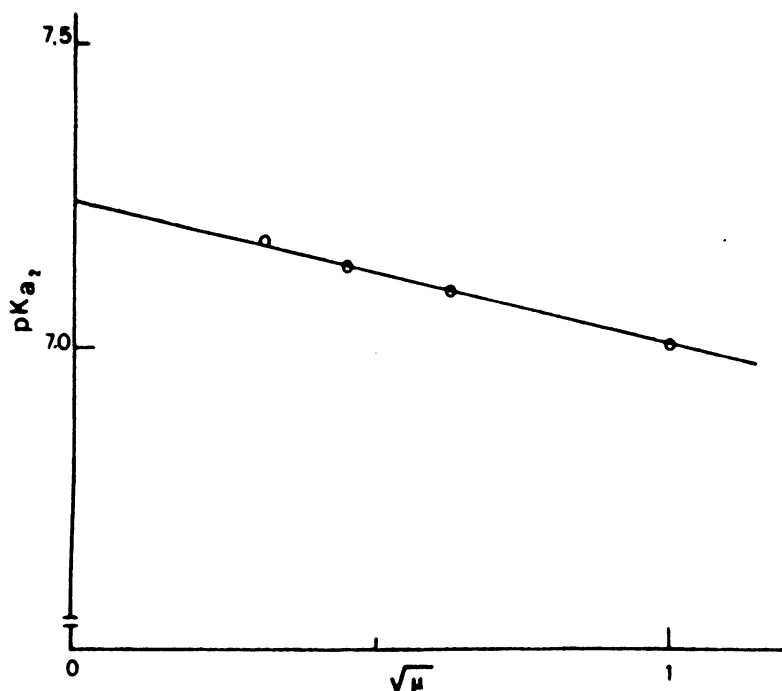| μ (M)	$\mu^{1/2}$	pK_{a_2}
0.1	0.316	7.18
0.2	0.447	7.14
0.4	0.632	7.10
1.0	1.00	7.01

FIG. 4. Variation of pK_{a_2} with ionic strength.

tromotive force measurements (E) of standard DNSHNa solutions (5.00×10^{-5}–1.00×10^{-2} M) containing sodium sulfate, for ionic strength adjustment, were carried out. All slopes were calculated by means of regression analysis on the linear part of the calibration curves (E vs log [DNSH$^-$]). The slope of the electrode ranged from 56.0 to 57.0 mV at ionic strength values from 0.006 to 0.6 M.

Evaluation of pK_{a_2}. Potential–pH curves at various DNSHNa concentrations and various ionic strengths were constructed. The pH of the initial solution was altered by addition of very small volumes (less than 0.2 ml per 20 ml of test solution) of sodium hydroxide or sulfuric acid solutions (Figs. 1 and 2). E_0 is the value of E in the pH range 2–6. From the values of potential and pH recorded, plots of $-\log (10^{(E - E_0)/S} - 1)$ vs pH were drawn for each ionic strength. The pK_{a_2} is equal to the intercept on the ordinate.

Evaluation of K_{inst} *of the [DNSFe]$^+$ complex.* A total of 25.00 ml of 2.0×10^{-4} M iron(III) solution at pH 2.5 was titrated with 2.0×10^{-4} M standard DNSHNa solution. These solutions contained the same amount of sodium sulfate for constant ionic strength adjustment. Measurements of e.m.f. were taken for any 0.5-ml titrant additions between 24 and 26 ml.

TABLE 2

Values of K_{inst} at Various Ionic Strengths

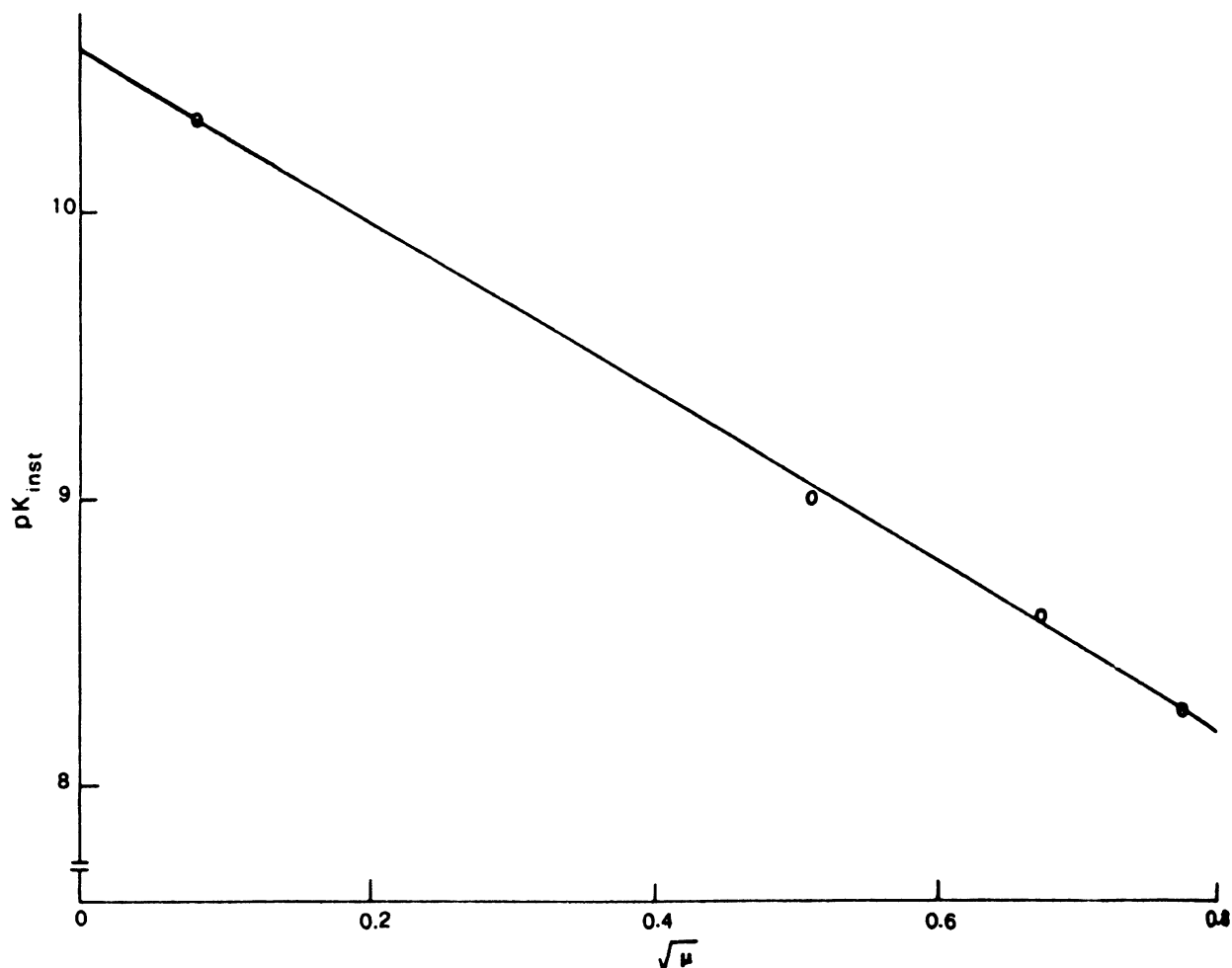| μ (*M*)	$\mu^{1/2}$	K_{inst}^a	pK_{inst}
0.006	0.08	4.79×10^{-11}	10.32
0.30	0.55	1.03×10^{-9}	8.99
0.45	0.67	2.49×10^{-9}	8.60
0.60	0.77	5.34×10^{-9}	8.27

a Average of five values.

FIG. 5. Variation of pK_{inst} with ionic strength.

Semiautomatic titration of thiourea (for the range 10^{-3}–10^{-2} M thiourea with 10^{-2} M $AgNO_3$). Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample and 2.00 ml of 10^{-2} M DNSHNa solution, start the stirrer and after the potential is stabilized ($\sim$1 min), start simultaneously the burette and the recorder to obtain the titration curve. For the greatest accuracy, calibrate the recorder for each titration, using the burette reading.

RESULTS AND DISCUSSION

The e.m.f. measurements of $DNSH^-$ solutions by the electrode at various pH levels after sulfuric acid or sodium hydroxide additions were plotted vs pH for different DNSHNa concentrations and constant ionic strength (μ = 0.2 M) (Fig. 1) or for different ionic strength values (μ = 0.1, 0.2, 0.4 and 1.4) and constant DNSHNa concentration (5.0 × 10^{-3} M) (Fig. 2). The sharp increase in potential at pH > 6 is due to a decrease of $DNSH^-$ ion concentration which is caused by a shift of the equilibrium between $DNSH^-$ and DNS^{2-}. In Fig. 3 are shown the plots of $-\log [10^{(E - E_0)/S} - 1]$ vs pH for the evaluation of pK_{a2} of $DNSS_2$ at different ionic strength values. Values of pK_{a2} at various ionic strengths calculated by the least-squares method are given in Table 1. These pK_{a2} values were plotted vs the square root at ionic strength (Fig. 4) yielding a value of pK_{a2} = 7.254 ± 0.0052 at zero ionic strength corresponding to an acid ionization constant of 5.57
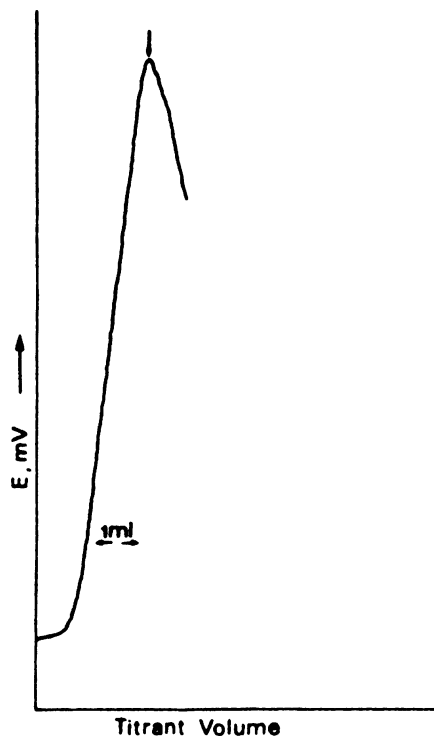
FIG. 6. Recorded curve for the semiautomatic potentiometric titration of 20.00 ml of thiourea (2.5 × 10⁻³ M) with silver nitrate (1.000 × 10⁻² M), in presence of DNSHNa; ↓, endpoint.

× 10⁻⁸ mol liter⁻¹. This value agrees closely with reported values (8). The agreement of the ionization constant with that found by other techniques indicates that the method is essentially sound. Furthermore, the use of ion-selective electrodes in the determination of equilibrium constants is proved as a useful technique.

In Table 2 are given the mean values of K_{inst} of the complex [DNSFe]⁺ at different ionic strengths, as calculated by Eq. (10). pK_{inst} values were plotted vs square root of ionic strength (Fig. 5) yielding a value of pK_{inst} = 10.57 ± 0.0001 at zero ionic strength, corresponding to an instability constant of 2.71 × 10⁻¹¹ (at 25 ± 0.2°C and pH 2.5). This value is in good agreement with that calculated using experimental data found in (9).

TABLE 3

Semiautomatic Potentiometric Titration of Thiourea with Silver
Nitrate in Presence of DNSHNa

Amount (μmol)		Error
Taken	Found	(%)
20.0	20.5	+2.5
30.0	30.4	+1.3
50.0	49.6	-0.8
70.0	70.0	—
100.0	99.7	-0.3
150.0	150.1	+0.1
200.0	201.8	+0.9
		Av. 0.8

3,5-Dinitrosalicylate, like picrate (2), gives precipitates with thiourea and silver. In the titration of thiourea with standard silver nitrate in the presᵒnce of 3,5-dinitrosalicylate ions, the water insoluble salt [Ag(SCN$_2$H$_4$)$_2$] (DNSH) is obtained. Therefore, the equivalent weight of thiourea is double the molecular weight (Fig. 6).

Analysis of aqueous thiourea solutions of known concentrations gave the results shown in Table 3.

ACKNOWLEDGMENT

REFERENCES

1. Bray, L. G., Dippy, J. F., Hughes, S. R. C., and Luxton, L. W., Chemical constitution and the dissociation constants of monocarboxylic acids. Part XVII. Ortho-effects in substituted salicylic acids. *J. Chem. Soc.*, 2405 (1957).

2. Diamandis, E. P., and Hadjiioannou, T. P., Titrimetric determination of thiourea and silver with a picrate ion-selective electrode. *Microch. Acta [Wien] II*, 255–260 (1977).

3. Hadjiioannou, T. P. and Diamandis, E. P., Analytical study of a new picrate-selective membrane electrode. *Anal. Chim. Acta* 94, 443–447 (1977).

4. Hadjiioannou, T. P., and Gritzapis, P.C., Development and analytical applications of a new liquid membrane 3,5-dinitrosalicylate-selective electrode. *Anal. Chim. Acta* 126, 51–56 (1981).

5. Koupparis, M. A., and Hadjiioannou, T. P., Evaluation of the chloramine-T membrane electrode response in acidic acid solutions. The determination of the pK_a of *m*-chloro-*p*-toluene sulfonamide (chloramine-T acid). *Microchem. J.* 23, 178–184 (1978).

6. Srinivasan, K., and Rechnitz, G. A., Reaction rate measurements with the fluoride ion selective electrode. Formation kinetics of ferrous fluoride and aluminum fluoride complexes. *Anal. Chem.* 40, 1818–1825 (1968).

7. Vandenborgh, N., Evaluation of the lanthanum fluoride membrane electrode response in acidic solutions. The determination of the pK_a of hydrofluoride acid. *Talanta* 15, 1009–1013 (1968).

8. Vassiliadis, C., Colovos, G., and Karayannidis, P., Determination of the second dissociation constant of 3,5-dinitrosalicylic acid. Stability of its copper complex in aqueous solutions. *Chim. Chron. A* 81, 46–50 (1966).

9. Vassiliadis, C., Manoussakis, G., and Colovos, G., Iron(III)-3,5 dinitrosalicylate complex. Spectrophotometric study. *Chim. Chron. A* 29, 322–325 (1964).