*The Absorption Spectra of Thiourea and Potassium Iodide on Nickel Metal**

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Organic or inorganic compounds are extensively used for corrosion inhibitors. Many interesting studies on the mechanism of corrosion inhibition have been reported; the chemical adsorption of organic compounds or inorganic ions on metal surfaces is considered to be the most important process.¹⁾ The great majority of works, however, have been gravimetric or electrochemical. Because these data do not directly furnish information about the interaction between inhibitor molecules or ions and metal surfaces, there has been much speculation on this point. Absorption sorption spectroscopy has proven to be one of the most powerful tools for studying intermolecular interaction. Absorption spectra of organic compounds adsorbed on silica or alumina have been studied by several investigators, and many interesting results have been published.²⁾ Inorganic surface complex formation on different adsorbents has also been revealed by diffuse reflection spectra.³⁾

Thiourea and the iodine ion are effective corrosion inhibitors. They have a very strong absorption band near 230 mμ, a band which facilitates the measurement of the spectrum of adsorbed species. Thiourea has the most simple structure in the homologue, and the potassium ion has no absorption band near 230 mμ. For these reasons thiourea and potassium iodide were chosen to investigate the mechanism of corrosion inhibition. In the present paper the absorption spectra of thiourea adsorbed on nickel surfaces and the diffuse reflection spectra of its solid complexes with some divalent metal salts will be reported on. The absorption spectra of the iodine ion on nickel surfaces in aqueous solutions will also be described.

Experimental

Absorption spectra were observed by means of a Hitachi EPU-2A photoelectric spectrophotometer. A diffuse reflectance attachment of the R-3 type was employed for the measurement of the diffuse reflection spectra of solid thiourea complexes. The spectral slit widths of the absorption and diffuse reflection spectra were 2 and 5 mμ respectively.

The reflection cells shown in Fig. 1 were used for measuring the absorption spectra of thiourea or the iodine ion adsorved on nickel. A light beam was reflexed twice at the nickel surfaces in the cell. Nickel of a 99.9% purity was used for the adsorbent and reflection mirror, since its ion in an aqueous solution has no remarkable absorption band in the observed region of the spectra and does not interfere with the measurement of the spectra of the inhibitors. The surfaces of nickel were polished with the 0/4 emery paper and with buff. The polished plates were then cleaned successively in dilute hydrochloric acid and pure water. The

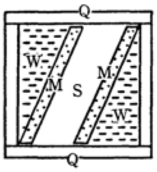

Fig. 1. Reflection cell.

M : Nickel plate
S : Solution
Q : Quartz window
W : Paraffin wax for fixing the nickel plate

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1) N. Hackerman and A. C. Mackrides, *Ind. Eng. Chem.*, **46**, 523 (1954).

2) A. N. Terenin, *Zhur. Fiz. Khim.*, **14**, 1111 (1940); M. Okuda and T. Tachibana, This Bulletin, **33**, 863 (1960).

3) G. Kortüm, *Trans. Faraday Soc.*, **58**, 1625 (1962).

TABLE I. EFFECT OF NICKEL SALT ON THE ABSORPTION BAND OF THIOUREA

Concn. of thiourea mol./l.	Salt		Solvent	λ_{max}, mμ	A_{max}
	Compd.	Concn. mol./l.			
6.0×10^{-5}	None	—	0.1 N H_2SO_4	236	0.785
	$NiSO_4$	1.0		234	0.762
5.0×10^{-5}	None	—	Water	236	0.608
	$NiSO_4$	0.030		236	0.619

Spectral slit width: 2 mμ
A: Absorbance

energies of light which had passed through a reflection cell filled with a solution and of light which had passed through the same cell filld with pure water were measured over the 215∼320 mμ region. The ratio of the energies gave an absorption curve. The lengths of the light path in the reflection cells were estimated from the intensity of a weak absorption band at 260 mμ of acetone of known concentrations. The concentrations of acetone were sufficiently high to avoid any significant change in the intensity of the band by adsorption.

Complexes of thiourea with cadmium, zinc and nickel chlorides were prepared by the method reported by Nardelli et al.[4] Fine particles of the complexes, the diameters of which were less than 40 μ, were collected for the diffuse reflectance measurement. No diluent was used so as to avoid any eventual change in the spectrum by adsorption on a diluent. Magnesium oxide was used as the reference standard.

Corrosion inhibitors are used in an acid solution. The surfaces of nickel are generally covered with an oxide layer which dissolves in acid. The absorption spectra were, therefore, observed in acid solutions for the most part.

Thiourea, acetone, potassium iodide, nickel chloride and sulfate, cadmium chloride, zinc chloride, hydrochloric acid and sulfuric acid of guaranteed grades were used in the experiments. Water was purified by distillation and ion exchange. Immediately after the purification, the specific electric conductivity of water was less than 2×10^{-7} mho/cm.

Results and Discussion

Thiourea. — The Absorption spectra of a thiourea solution as measured with a reflection cell and an absorption cell are shown in Fig. 2. In this figure a considerable intensity decrease in a band at 236 mμ in the reflection spectrum can be clearly seen. It is considered that nickel or nickel oxide on the surfaces of metal plates is dissolved in the dilute acid solution used in the experiment, though the dissolved quantity might be very small, and that the nickel ion in the solution can form complexes with thiourea. The absorption band of thiourea may change in its position and intensity upon complex formation. The hypothesis that the observed intensity decrease arose from the complex formation in the solution might be postulated. The absorption spectra of thiorurea in acid or in water with or without nickel salt were also observed (Table I). The change in the intensity of the absorption band upon the addition of salt is very small and can be considered to be within the limit of experimental error. A slight blue shift of band was observed only for a solution containing salt in a high concentration. The hypothesis can, therefore, be ruled out from the results of the experiments mentioned above.

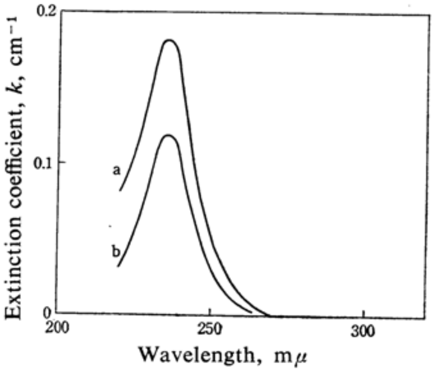

Fig. 2. Absorption spectra of thiourea.

a : Transmission measurement
b : Reflection measurement
Solvent: 0.001 N HCl

An intensity decrease in the absorption band upon adsorption has been reported by some investigators.[5] At first sight, the intensity decrease observed in the present work may be considered to be one example of this phenomenon. The observed reduction in intensity, however, seems to be too large to be regarded as the result of an intensity change upon adsorption, since the number of thiourea molecules in the solution is probably larger than that on nickel surfaces and since the

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[4] M. Nardelli, L. Cavalca and A. Braibanti, *Gazz. chim. ital.*, **86**, 867, 1037 (1956).

[5] M. Robin and K. N. Trueblood, *J. Am. Chem. Soc.*, **79**, 5138 (1957); H. Kobayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1399 (1959); K. Fueki, K. Hirota and H. Otouma, Paper presented at the 15th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1962.

contribution to the intensity of the absorption band from the molecules in solution should be larger than that from the molecules on nickel surfaces. Furthermore, the intensity decrease upon adsorption is generally accompanied by a change in band shape, and the bands of adsorbed molecules are diffuse.[5] The absorption band observed with the reflection cell has the same shape as that observed with the absorption cell, as Fig. 2 shows. It is difficult, therefore, to deduce that the observed intensity decrease was caused by the reduced intensity of the absorption band of adsorbed molecules.

The structure of thiourea and of a number of its complexes with divalent metal salts was studied with infrared absorption spectra and X-ray diffraction techniques. These studies have shown that sulfur-to-metal bonds are formed in these complexes.[6] The interatomic distance between sulfur and its nearest neighbors in the crystals was determined by the X-ray diffraction method. A value of 2.45 Å was calculated for the distance between sulfur and the cadmium atom in a thiourea-cadmium chloride complex,[7] and the distance of 3.45 Å was reported for the intermolecular contact between sulfur and the amino group in a thiourea crystal.[8] The observed interatomic distance between sulfur and cadmium is almost equal to the sum of the covalent radii, 2.52 Å.[9] The interatomic distance between sulfur and hydrogen in a thiourea crystal can be estimated to be larger than 2.45 Å, because the length of the N-H bond is about 1.0 Å. The sum of the covalent radii of sulfur and hydrogen is 1.34 Å,[9] which is considerably shorter than the estimated distance. The intermolecular perturbation to the thiocarbonyl group can, therefore, be deduced to be larger in the complex than in thiourea.

The diffuse reflection spectra of thiourea and its complexes with cadmium, zinc and nickel chlorides in the form of fine powder were observed. The obtained results are shown in Fig. 3, except for the spectrum of the thiourea-nickel chloride complex, in which an absorption band at a longer wavelength due to thiourea was difficult to isolate because of overlapping with a strong absorption band of nickel. A diffuse reflection spectrum of cadmium chloride is also shown in this figure for the sake of comparison. The bands near 250 mμ of complex crystals are considered to correspond to a band at 273 mμ of thiourea. This blue shift of the band is probably caused by the perturbation of electronic states through the sulfur atom. In this connection, a blue shift of the band at 236 mμ of thiourea in solution upon adsorption on nickel surfaces can be expected, because in acid solutions protons attach to amino groups and the sulfur atom may play an important role upon adsorption.[10]

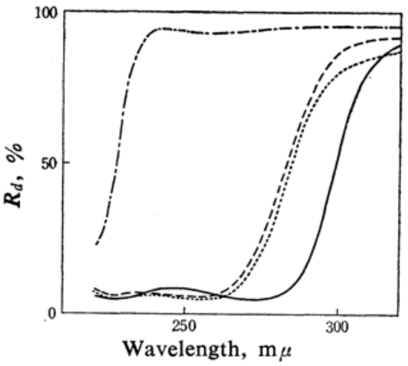

Fig. 3. Diffuse reflection spectra of thiourea and its complexes.

——— Thiourea
– – – Thiourea-$CdCl_2$ complex
········ Thiourea-$ZnCl_2$ complex
—·—· $CdCl_2$
Particle size; $d \leqq 40\ \mu$

The concentration of adsorbed thiourea was estimated on the assumption that the absorption band of adsorbed molecules shifted to the unobserved region of shorter wavelengths (Table II). A roughness factor of 2 was assumed in the calculation, since the surfaces were polished mechanically. On the other hand, nickel plates were dipped in solutions of thiourea for several minutes. After the plates had been withdrawn, the solutions were subjected to the measurement of the absorption spectrum. The results obtained are shown in Table III. The reproducibility of the experiment is rather poor, but a remarkable intensity decrease is clearly seen. The reduction in intensity can be considered to be caused by the removal of thiourea adsorbed on nickel from the solution. The values of the concentration of adsorbed molecules on dipped nickel surfaces calculated with the assumption of the same roughness factor, values which are shown in Table III, are in fairly good agreement with the values shown in Table II. The agreement of the

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[6] M. Nardelli, *Gazz. chim. ital.*, **89**, 1616 (1959); M. Brufani, D. Duranti, G. Giacomello and L. Zambonelli, ibid., **91**, 287 (1961); A. Yamaguchi, R. B. Penland, S. Mizushima, J. T. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

[7] L. Cavalca, M. Nardelli and A Braibanti, *Gazz. chim. ital.*, **87**, 137 (1957).

[8] R. W. G. Wycoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

[9] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca (1940), p. 179.

[10] W. Suëtaka and S. Shimodaira, *Sci. Rept. Res. Inst., Tohoku Univ., Ser. A*, **15**, 313 (1963).

TABLE II. TRANSMISSION AND REFLECTION MEASUREMENT OF ABSORPTION SPECTRUM OF THIOUREA

Concn. of thiourea mol./l.	Method	k_{max} cm^{-1}	Vol. of soln. cc.	App. surface area cm^2	Concn. of adsorbed molecules mol./cm^2
1.4×10^{-5}	Trans.	0.180	—	—	—
	Ref.	0.108	1.0	7.8	3.6×10^{-10}
		0.116	1.2	7.4	4.0×10^{-10}
1.4×10^{-5}	Trans.	0.174	—	—	—
	Ref.	0.106	1.2	7.4	4.4×10^{-10}
6.1×10^{-5}	Trans.	0.796	—	—	—
	Ref.	0.699	1.2	7.4	4.9×10^{-10}

Spectral slit width: 2 mμ
Solvent: 1/1000 N HCl
k: Extinction coefficient

TABLE III. CONCENTRATION OF THIOUREA ADSORBED ON NICKEL PLATES

Concn. of thiourea mol./l.	A_{max}	Vol. of soln. cc.	App. surface area cm^2	Concn. of adsorbed molecules mol./cm^2
1.7×10^{-5}	a*: 0.201	—	—	—
	b**: 0.144	3.0	15	4.4×10^{-10}
1.4×10^{-5}	a: 0.174	—	—	—
	b: 0.126	3.0	22	2.7×10^{-10}
6.1×10^{-5}	a: 0.796	—	—	—
	b: 0.689	3.0	24	4.2×10^{-10}

* a: Before dipping the nickel plates
** b: After withdrawal of plates
Solvent: 1/1000 N HCl

TABLE IV. TRANSMISSION AND REFLECTION MEASUREMENT OF ABSORPTION SPECTRUM OF POTASSIUM IODIDE

Solvent	Concn. of KI mol./l.	Method	λ_{max} mμ	k_{max} cm^{-1}
H_2O	1.2×10^{-5}	Trans.	226	0.147
		Ref.	226	0.142
H_2O	2.4×10^{-5}	Trans.	226	0.328
		Ref.	226	0.329
0.002 N HCl	2.4×10^{-5}	Trans.	226	0.358
		Ref.	227	0.301
0.001 N H_2SO_4	2.4×10^{-5}	Trans.	226	0.353
		Ref.	227	0.291
0.002 N H_2SO_4	2.2×10^{-5}	Trans.	226	0.303
		Ref.	227	0.250

Spectral slit width: 2 mμ

calculated concentrations can be considered to support the hypothesis that the intensity decrease observed in the reflection spectra arose from the large blue shift of the absorption band upon adsorption.

The decomposition of thiourea on nickel surfaces should be taken into account. It is believed, however, to be of small importance, because, as can be seen from Table II, the concentration of thiourea on nickel surfaces did not vary with the change of concentration in the solution. A more conclusive result would be obtained from research into the absorption spectrum of adsorbed thiourea in the shorter wavelengths, which could not be measured in the present work.

Potassium Iodide.—The results of the absorption spectrum measurement of potassium iodide obtained with the reflection cells are collected in Table IV. In this table, the results of normal absorption measurement are also shown. While a remarkable intensity reduction of the charge transfer band of the iodine ion at 226 mμ in reflection measurements was observed for acid solutions, no important change was seen for solutions in pure water. Nickel plates could be attacked by the acid solution used to a slight extent, and the resulting nickel ions in the solution might cause an intensity decrease of the absorption band. The absorption spectrum of potassium iodide in a dilute (1×10^{-3} N) sulfuric acid aqueous solution containing nickel sulfate in the concentration of 7×10^{-4} mol./l. was observed in the 200∼320 mμ region. The addition of the nickel salt caused only a negligible reduction in the intensity of the band at 226 mμ. These facts suggest that, while a strong interaction can be expected between the iodine ion and the nickel surface in acid solutions, the interaction should be very small in pure water. A new absorption band was observed at 310 mμ in the reflection measurement of acid solutions (Fig. 4). The nickel ion in an acid aqueous solution, the concentration of which is as high as 1.0 mol./l., does not show an absorption band at the same wavelength. This band may arise from nickel atoms on the metal surfaces or from a surface complex formed on the nickel plates, but it is premature to advance a discussion of this point.

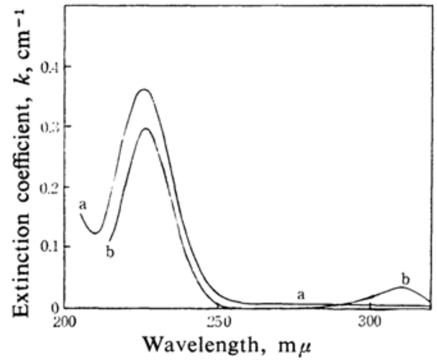

Fig. 4. Absorption spectra of potassium iodide.

a : Transmission measurement
b : Reflection measurement
Solvent : 0.001 N H_2SO_4

Summary

The absorption spectra of thiourea molecules adsorbed on nickel surfaces in acid aqueous solutions have been observed by means of reflection cells. A new band did not appear in the observed region, but the intensity of the absorption band at 236 mμ decreased remarkably. The absorption spectra of potassium iodide have also been observed with reflection cells. For acidic solutions an absorption band at 226 mμ decreased in intensity and a new band appeared at 310 mμ, while for the solutions in pure water no change in the spectrum has been observed. The observed results have been discussed and a hypothesis of surface complex formation presented.

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