

Discussion of “Adsorption of Thiourea and its Derivatives at the In-Hg/Electrolyte Interface.” [R. Narayan and N. Hackerman (pp. 1426–1430, Vol. 118, No. 9)]

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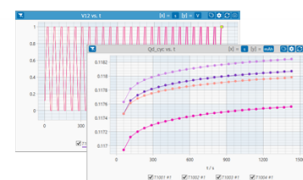
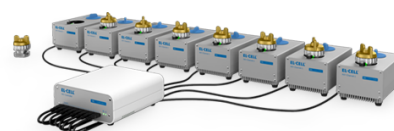
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parts of the membranes, since the back is subjected to anodic treatment?

One would expect these experiments to be made at room temperature. Why was a temperature of 50° and 60°C used, and in one case 70°C?

On page 1116 of the paper by Bockris and Subramanyan there is a discussion of "H damage." Hydrogen is sometimes referred to as H_2 . Is the H in "H damage" merely H_2 , and could the expression just as well be " H_2 damage," or is a different form of hydrogen intended to be indicated by the plain "H"?

This writer feels that the results of these experiments are due to the porosity of the membranes, and not to hydrogen diffusion at all. Gross porosity of the membranes could readily be checked by the method which has been suggested² of reversing the polarity of the charging current on the front of the membrane and seeing if there is an immediate change in the polarity of the back of the membrane. This method depends upon the presence of thin threads of solution through the capillaries in the metal of the membrane, from front to back.

If the capillaries in the metal of the membrane are small enough and few enough, it is conceivable that the threads of solution in them might make a poor and irregular connection from the front to the back of the membrane which could easily be broken as by hydrogen bubbles, and easily be re-established when the current was shut off as during the decay tests shown in Fig. 3 and 4 in the paper under discussion. Such re-establishment of solution connections would permit any residual cathode polarization on the front of the membrane to affect the potential on the back, and this would be an explanation of the effects noted in Fig. 3 and 4.

The closely-connected report of Beck, Bockris, Genshaw, and Subramanyan³ is also of considerable interest. The solubility of hydrogen in nickel is given as almost 1000 times the solubility in iron, and yet the permeability of iron-nickel alloys falls to about one thousandth of that of iron at about 40% or more of nickel. This contradiction does not seem adequately explained.

An excellent correlation is noted between the permeability of the membranes and their corrosion resistance, the membranes with 40% or more of nickel having about 1000 times the corrosion resistance of iron. The authors suggest that the higher permeability of iron may be due to the formation of pits caused by corrosion and the spreading of cracks to the surface. Is not this tantamount to saying that iron membranes may become more porous than 40% nickel membranes due to corrosion, and that the permeability of iron membranes in which hydrogen is less soluble, is due to porosity?

The writer again wishes to bring into question the validity of the method proposed by Devanathan, Stachurski, and Beck⁴ for determining the permeability of metal membranes to hydrogen.

Adsorption of Thiourea and its Derivatives at the In-Hg/Electrolyte Interface.

R. Narayan and N. Hackerman (pp. 1426-1430, Vol. 118, No. 9)

A. N. Frumkin and N. B. Grigoryev:⁵ Starting from 1928⁶ the adsorption of thiourea at the metal/electrolyte solution interface has attracted the attention of electrochemists as an example of a reversible adsorption process resulting from a chemisorptive interaction

³ W. Beck, J. O'M. Bockris, M. A. Genshaw, and P. K. Subramanyan, *Metallurgical Transactions*, **2**, 883 (1971).

⁴ M. A. V. Devanathan, Z. Stachurski, and W. Beck, *This Journal*, **110**, 886 (1963).

⁵ Institute of Electrochemistry, Academy of Sciences of the U.S.S.R., Moscow.

⁶ A. Frumkin, *Ergeb. Exakt. Naturw.*, **7**, 235 (1928); *Coll. Symp. Ann.*, **7**, 89 (1930).

of the functional group and the metal surface. This problem is also treated in the interesting paper under discussion of Narayan and Hackerman, who considered the case of thiourea adsorption on indium amalgams.⁷ The aim of this note is to fill up some gaps in their paper.

Adsorption of thiourea leads to a shift of pzc towards negative potentials, which is due to the orientation of the C-S bond with the negatively charged sulfur atom to the metal surface. This conclusion, first obtained from electrocapillary curves,⁸ was confirmed by the determination of pzc from the minimum on the C,E curves in diluted electrolyte solutions.⁹ Analysis of these curves showed that unlike the desorption maxima of many aliphatic and aromatic compounds, the desorption maximum for solutions with thiourea additions is due to the strong shift of pzc in the negative direction, rather than to the effect of thiourea on the double layer capacity. The adsorption of thiourea on a dropping gallium¹⁰ and on a lead electrode was investigated.^{11,12} The adsorption potential shifts on gallium are greater, and on lead smaller, than on mercury. Experimental data on thiourea adsorption on mercury⁹ and gallium¹¹ were used for verification of the theory of the discrete double layer at the metal/solution interface in the presence of specific adsorption of dipole molecules and adsorption of solvent molecules.¹³ The Esin-Markov coefficient, calculated with the use of reasonable values of the double layer parameters, agreed well with the experimental values and, in conformity with the theory, decreased when passing from mercury to gallium.

It was shown¹⁴ that the influence of thiourea adsorption on the kinetics of electrochemical processes on mercury and on thallium amalgams can be well accounted for by taking into consideration the ψ -effect. Meurée and Gierst¹⁴ described for the first time the interesting phenomenon, which is also considered in the paper under discussion, viz., the appearance of sharp peaks on the C,E curves during simultaneous adsorption of thiourea and halogen ions. Such sharp peaks point to a drastic change of the surface charge in a narrow potential range and to the presence of attractive interactions between adsorbed particles at more positive potentials. Narayan and Hackerman, in the paper under discussion, suppose that in this case at anodic potentials thiourea molecules turn towards the amalgam surface with their positive nitrogen end. We think that, considering that urea shows practically no surface activity at the mercury/solution interface,⁶ this concept is unlikely. However, this problem cannot be cleared up without a more thorough examination of the characteristics of the adsorption layer of thiourea in the presence of halogen ions. The C,E curves with such peaks were obtained at our laboratory during thiourea adsorption on mercury in the presence of I^- , but we decided not to publish them until they could be investigated in more detail.

⁷ The choice of indium amalgams as adsorbent is perhaps not optimum owing to the change in the surface layer composition with changing potential. In the quantitative interpretation of this dependence there are some discrepancies between Butler's results, which are used by Narayan and Hackerman, and those obtained by Frumkin et al.⁶ We shall not dwell on this problem here since recently it was thoroughly dealt with.

⁸ A. Frumkin, N. Polianovskaya, I. Bagotskaya, and N. Grigoryev, *J. Electroanal. Chem.*, **33**, 319 (1971).

⁹ A. Morozov, N. Grigoryev, and I. Bagotskaya, *Elektrokhimiya*, **3**, 585 (1967).

¹⁰ On a stationary gallium electrode¹¹ in the presence of thiourea, the capacity was found to depend on the a-c frequency and on the age of the electrode/solution interface, which points to a slow chemical interaction of gallium with thiourea (with a dropping gallium electrode such phenomena are not observed). In this connection it would perhaps be useful to carry out measurements with a dropping In-Hg electrode.

¹¹ I. Bagotskaya, S. Fateev, N. Grigoryev, and N. Bardina, *Elektrokhimiya*, **6**, 369 (1970); N. Grigoryev, S. Fateev, and I. Bagotskaya, *ibid.*, **7**, 223 (1971).

¹² N. Grigoryev and D. Machavariani, *ibid.*, **6**, 89 (1970).

¹³ N. Grigoryev and V. Krylov, *ibid.*, **4**, 763 (1968); V. Krylov and N. Grigoryev, *ibid.*, **7**, 511 (1971).

¹⁴ N. Meurée and L. Gierst, *Collection Czech. Chem. Commun.*, **36**, 389 (1971); Extended Abstracts 21st CITCE Meeting Praha (1970).

Finally we should like to mention that there are rather numerous data in literature^{15,16} on the effect of thiourea and its derivatives as corrosion inhibitors, mentioned in the paper under discussion.

R. Narayan and N. Hackerman: We thank the authors of the above discussion for bringing to our attention the extensive Russian literature on the subject. However, our paper was presented at the 1967 October meeting of The Electrochemical Society held in Chicago, and triangular correspondence across 10,000 miles delayed the publication. So, in effect, the paper was written prior to the appearance of the recent references noted by Frumkin and Grigoryev. Therefore, the recent references were not included.

There are at least two points of major difference between the results of Butler^{17,18} and that of the Russian school:¹⁹ (i) variation of the negative surface excess of indium with the potential calculated from electrocapillary measurements and (ii) the presence of the hump in the capacitance curves. Our measurements show the second observation and the results are in general agreement with those of Butler.

The sharp peaks in the capacitance curves in the presence of thiourea and chloride ions could be observed only with the amalgam electrodes of 20 mole per cent In or more. The negative surface excess of indium also shows a maximum at this concentration^{17,18} and hence this result was emphasized. However, the suggestion by Frumkin and Grigoryev regarding possibility of compound formation was also included.

The literature²⁰ available shows that thiourea invariably enhances the double-layer capacitance for the Hg, Pb, and Ga electrodes. Our results show that with In-Hg electrodes there is a region of potentials in which the capacitance is depressed by the presence of thiourea. A transition hump is also obtained with amalgams of higher indium concentrations. This hump apparently becomes a peak in the presence of chloride ions. The mechanism for the peak formation is not clear. As Frumkin and Grigoryev point out strong attractive interactions come into play. Our suggestion was that the adsorbed anions reduce the mutual repulsions between adsorbed thiourea species and that the positive end of the dipole may be oriented towards the amalgam. This suggestion is based on the fact that interfacial composition of indium increases with positive polarization. The absence of surface activity of urea at the Hg solution interface probably indicates the absence of Hg-N interaction. Would this also mean the absence of In-N interaction?

An important fact which we did not consider was that thiourea is present to a large extent as the protonated species in acid solutions. The proton is attached to the sulfur atom. We have evidence of this based on studies with Fe and Hg electrodes in solutions of varying pH containing thiourea and N-substituted thioureas.²¹ What would be the nature of the metal-thiourea interaction under these conditions? It is also worthwhile carrying out investigations with a dropping amalgam electrode.

We described perhaps for the first time the appearance of peaks in the C-E curves during simultaneous adsorption of thiourea and chloride ions, when presenting the paper in Chicago. Gierst and co-worker

observed such peaks in the presence of bromide ions. Frumkin and Grigoryev claim such observations in the presence of iodide ions. Recent studies in the Indian Institute of Technology, Madras, by tensammetry showed that such peaks, rather small and sharp, can be obtained in the presence of chloride ion also using a d.m.e. The minimum chloride ion concentration corresponds to 0.25M KCl or 0.2M HCl. Further work is in progress.

The reference in our paper regarding data on corrosion inhibition was only an illustration of work which emphasizes the cumulative effects of anion and thiourea derivatives on the process of corrosion.

The Electrochemical Behavior of Technetium and Iron Containing Technetium.

G.H. Cartledge (pp. 1752-1758, Vol. 118, No. 11)

S. Trasatti:²² In the paper under discussion, the author reports the value of about $9 \times 10^{-5} \text{ A cm}^{-2}$ for the exchange current of the electrolytic hydrogen evolution reaction on Tc. To my knowledge, this is the first measurement of this kind reported for Tc, a metal for which data regarding surface properties are indeed almost nonexistent. As an example, in the most recent review by Hayward²³ on chemisorption from the gas phase, Tc is tabulated always in brackets because of lack of any data for characterization. At first sight, it would therefore appear impossible to ascertain the reliability of the $i_{0,H}$ value reported by Cartledge, without repeating experimental measurements. However, I will here attempt to undertake this task by making use of a number of correlations I have recently developed²⁴⁻²⁷ between electrochemical properties and work function of metals. Conversely, this attempt, if positive, will constitute in turn a valuable test of the reliability of such correlations originally devised to predict unknown properties of metals or metallic materials.

The ground datum from which this analysis will start is the value of Pauling's electronegativity,²⁸ (x_M). Recent considerations²⁶ show that Pauling's values are generally dependable also in the case of less common metals. Correlation exists between x_M and the work function ϕ which in the case of transition metals is expressed by the equation²⁶

$$x_M = 0.50\phi - 0.55 \quad [1]$$

Using for Tc $x_M = 1.9$, we obtain $\phi = 4.9 \text{ eV}$. Now, this value can in turn be used in the correlation between $i_{0,H}$ and ϕ which, for transition metals, is given²⁷ by

$$\log i_{0,H} = 6.7\phi - 36.6 \quad [2]$$

Thus, from Eq. [2] the value of $1.6 \times 10^{-4} \text{ A cm}^{-2}$ is derived for $i_{0,H}$ of Tc. In view of the factors which may affect exchange current measurements and the fact that the value of x_M given by Pauling is approximate to the first figure^{26,28} the agreement between observed and calculated values of $i_{0,H}$ for Tc can be considered as very satisfactory. It may be noted that coincidence of the two values is obtained with a x_M value of 1.88. Once established that the $i_{0,H}$ obtained by Cartledge is basically correct, it is more reasonable to refine the value of x_M from the experimental value of $i_{0,H}$ than the reverse, as the experimental uncertainty of electrochemical measurements is intrinsically lower than that pertaining to x_M values as claimed by Pauling.²⁸

²² Laboratory of Electrochemistry, the University, Milan, Italy.

²³ D. O. Hayward, in "Chemisorption and Reactions on Metallic Films," Vol. 1, J. R. Anderson, Editor, Academic Press (1971).

²⁴ S. Trasatti, *Chim. Ind. (Milan)*, **53**, 599 (1971).

²⁵ S. Trasatti, *J. Electroanal. Chem.*, **33**, 351 (1971).

²⁶ S. Trasatti, *J. C. S. Faraday I*, **68**, 229 (1972).

²⁷ S. Trasatti, *J. Electroanal. Chem.*, Submitted for publication.

²⁸ L. Pauling, "The Nature of the Chemical Bond," University Press, Ithaca (1960).

¹⁵ Z. Jofa, 2-ème Sympos. Europ. sur les Inhib. de Corros., Ferrara, 1966, p. 93; Z. Jofa and G. Tomashova, *Zh. Fiz. Khim.*, **34**, 1036 (1960); Z. Jofa, *Zashchita Metal.*, **6**, 491 (1970).

¹⁶ L. Cavallaro, L. Felloni, G. TrabANELLI, and F. Pulidori, *Elettrochim. Acta*, **8**, 521 (1963); L. Cavallaro, L. Felloni, G. TrabANELLI, and F. Pulidori, *ibid.*, **9**, 485 (1964); L. Cavallaro, L. Felloni, G. TrabANELLI, and F. Zucchi, 2-ème Sympos. Europ. sur les Inhib. de Corros., Ferrara, 1966, p. 417.

¹⁷ J. N. Butler, M. L. Meehan, and A. C. Makrides, *J. Electroanal. Chem.*, **9**, 237 (1965).

¹⁸ J. N. Butler, *J. Phys. Chem.*, **69**, 3817 (1965).

¹⁹ E. V. Yakovleva and N. V. Nikolaeva Fedorovich, *Soviet Electrochem.*, **6**, 29 (1971).

²⁰ *Ftn.*, **8**, 9, 11, 12, 13 (English translation).

²¹ R. Narayan and K. Chandrasekara Pillai, *Trans. of SAEST, India* (April-June), In press.