Electrode Kinetics of Indium(III) at the Dropping Mercury Electrode

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The polarographic behavior of indium(III) has been investigated in various media by many authors. In these investigations two typical electrode processes are noticeable: One is a reversible process which proceeds at about −0.5 V. vs. S. C. E. in the chloride, bromide, iodide or organic acid solution[1,2]. The other is an irreversible process which proceeds at about −1.0 V. vs. S. C. E. in the perchlorate[2] or phosphate[3] solution*. In this report is presented the evaluation of the rate constant of the irreversible electrode process of indium(III) in the perchlorate medium, and the temperature dependence of the rate constant is discussed.

Experimental

The apparatus used was described in the previous report[4] and was not modified in any detail.

All the reagents were of analytical grade. The stock solution of indium perchlorate was prepared by dissolving indium oxide (weighed as $In_2O_3 \cdot 3H_2O$) in perchloric acid. Indium oxide was prepared from indium chloride by precipitating indium hydroxide with ammonium hydroxide and by desiccating the precipitate to a constant weight at 130°C.

In order to avoid the overlap of the hydrogen wave on the indium wave, the hydrogen-ion concentration was controlled by adding sodium hydroxide. The concentration of the perchlorate ion in the test solution was 0.5 F.

Purified nitrogen was bubbled to remove dissolved oxygen in the test solution prior to submission to polarography.

The temperature was kept constant within the change of ±0.1°C by a thermostat.

Results and Discussion

Irreversible Current-Voltage Curve of Indium(III).—The irreversible current-voltage curve of indium(III) in the perchlorate medium is illustrated in Fig. 1. Usually, this irreversible wave is accompanied by a pronounced maximum of the first kind. This maximum wave can be suppressed by the addition of a surface active material such as gelatine, methyl red or methyl cellulose. The adsorption of the surface active material on the surface of the dropping mercury electrode (DME), however, seems to change the potential distribution on and near the electrode surface, and this effect results in the variation of the transfer coefficient[3,5]. Moreover, the adsorptive concentration will vary with the change of temperature. Accordingly, the use of a surface active material is not desirable for the purpose of investigating

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[1] J. Heyrovsky, *Chem. Listy*, **19**, 168 (1925); S. Takagi, *J. Chem. Soc. London*, 301 (1928); J. Tomes, *Collection Czechoslov. Chem. Communs.*, **9**, 12 (1937); J. A. Schufle, M. F. Stubbs and R. Witman, *J. Am. Chem. Soc.*, **73**, 1013 (1951); Z. S. Mukhina, *Zavodskaya Lab.*, **14**, 354 (1948); G. Reinacher and E. Hoschek, *Z. anorg. u. allgem. Chem.*, **268**, 260 (1952); F. Ensslin, *Metall u. Frg.*, **38**, 305 (1941), *Chem. Abstr.*, **36**, 6107 (1942); M. Bulovova, *Collection Czechoslov. Chem. Communs.*, **19**, 1123 (1954).

[2] J. J. Lingane, *J. Am. Chem. Soc.*, **61**, 2099 (1939).

[3] H. Imai, *J. Sci. Hiroshima Univ.*, **A22**, 291 (1958).

* H. Nakatani has reported that both of the two electrode processes can be observed in one polarogram in the acetic acid—ammonium acetate buffer, and that the second wave is more pronounced with the addition of gelatine [*J. Sci. Hiroshima Univ.*, **A19**, 183 (1955); ibid., **A20**, 49 (1956)].

[4] H. Imai, This Bulletin, **30**, 873 (1957).

[5] P. Delahay and J. E. Strassner, *J. Am. Chem. Soc.*, **73**, 5219 (1951); H. Imai and S. Chaki, This Bulletin, **29**, 498 (1956).

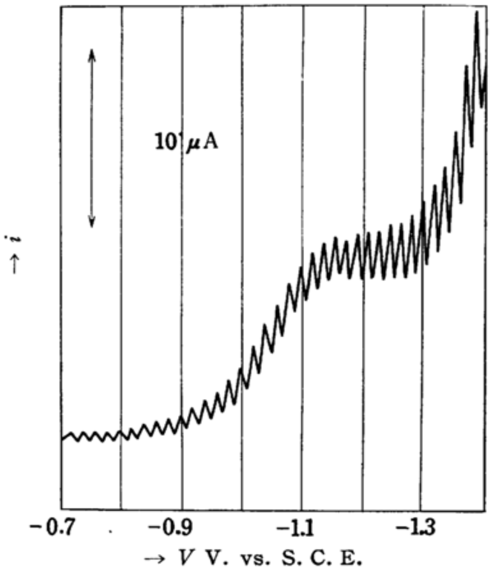

Fig. 1. The current-voltage curve of indium(III) in 0.5 F perchlorate. Temp.=20°C, $m=1.8_1$, $t=4.9_0$ (open circuit), $[In^{3+}]=1$ mF.

the temperature dependence of the reaction rate. In this experiment, the life-time of the DME was elongated by lowering the mercury head, and the supporting electrolyte was appreciably concentrated. Under these conditions, the maximum wave could be satisfactorily minimized. The test solution may be contaminated by the trace of surface active materials which have been accidentally intermixed. After this trace was removed by adding active charcoal, the maximum could not be suppressed in any way. The presence of this trace, however, scarcely affects the value of the transfer coefficient in the temperature range examined, as is illustrated in Table I.

When the hydrogen-ion concentration was too small, the test solution became turbid owing to the formation of indium hydroxide. Even when perchloric acid was added until the turbidity had just disappeared, the current-voltage curve of indium was too greatly extended, from −0.5 to −1.3 V. vs. S. C. E. On the other hand, when the acidity was too great, the hydrogen wave overlapped on the indium wave in question. Therefore, the perchloric acid concentration as great as 0.04 F was preferable.

Evaluation of Diffusion Constant. — The value of the diffusion constant of the indium ion is required for the calculation of the rate constant. This value was evaluated from the diffusion-controlled limiting current by Ilkovic's equation, i. e.

$$D^{1/2}=i_d/607\ nCm^{2/3}t^{1/6} \qquad (1)$$

where D is the diffusion constant in cm²/sec., i_d is the mean diffusion-controlled current in μA, n is the number of electrons transferred per an ion, C is the bulk concentration of indium(III) in mF, m is the average mass of mercury flowing in mg./sec. and t is the life-time of the DME in sec. The evaluation of the number of electrons transferred per an ion was carried out as follows: When chloride, iodide or acetate was added to the test solution, the irreversible wave was changed to the reversible one, the half-wave potential being simultaneously changed from −1.0 to −0.5 V. vs. S. C. E. It was confirmed that the diffusion-current constants of the two waves were practically equal[3]. In the reversible electrode process the value of n was evaluated to be three from the inclination of the $\log[i/(i_d-i)]$ versus E (the potential of the DME) plot. Accordingly, the value of n in the irreversible electrode process will also be three. The evaluated value of the diffusion constant is given in Table I.

Evaluation of Transfer Coefficient and Rate Constant.—The value of $\log[i/(i_d-i)]$ was plotted versus the potential of the DME from the irreversible current-voltage curve. This polt gave a straight line near the half-wave potential. According to Matsuda and Ayabe's theory[6], the inclination of the linear portion of this plot is a function of the transfer coefficient as is given in Eq. 2, i. e.

$$E=\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\{2.3\ \log(k_f^\circ f^\circ\ t^{1/2}D^{-1/2}) \\ -0.12-2.2\ \log[i/(i_d-i)]\} \qquad (2)$$

where f° is the activity coefficient of the depolarizer in the solution and the other symbols are used with their usual significance. The evaluated value of αn, which is the product of the transfer coefficient by the number of electrons involved in the rate-determining reaction, is illustrated in Table I.

The rate constant, k_f°, referred to 0 V. vs. N. H. E. was evaluated from Eq. 3[6], i. e.

$$E_{1/2}=\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}[2.3\ \log(k_f^\circ f^\circ D^{-1/2}) \\ +1.15\ \log t-0.12] \qquad (3)$$

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[6] H. Matsuda and Y. Ayabe, This Bulletin, 28, 422 (1955).

where $E_{1/2}$ is the half-wave potential of the irreversible wave in volts vs. N. H. E. The values of the rate constant at various temperatures ranging from 20 to 30°C are illustrated in Table I.

TABLE I. THE DIFFUSION CONSTANT, THE TRANSFER COEFFICIENT AND THE RATE CONSTANT OF THE ELECTRODE PROCESS OF INDIUM-(III) IN 0.5 F PERCHLORATE

Temperature T°K	Diffusion constant D, cm²/sec.	Transfer coefficient αn	Rate constant k_f°, cm./sec.
293.2	8.0×10^{-6}	0.66	2.2×10^{-12}
299.7	9.6×10^{-6}	0.66	4.7×10^{-12}
303.2	10.8×10^{-6}	0.65	7.3×10^{-12}

Temperature Dependence of Rate Constant.—From Table I, the logarithm of the rate constant was plotted versus the reciprocal of the absolute temperature. This plot is satisfactorily linear as is illustrated in Fig. 2. From the inclination of this plot, the heat of activation at constant pressure (ΔH^*) was calculated by Arrhenius's equation, i. e.

$$\mathrm{d}\ln k_f^\circ/\mathrm{d}t=\Delta H^*/\boldsymbol{R}T^2 \quad \text{or}$$

$$\log k_f^\circ = c-\Delta H^*/2.3\ \boldsymbol{R}T \tag{4}$$

where c is a constant. The heat of activation at constant volume ($\Delta H^{\neq}$) was calculated by Eq. 5 in order to apply the absolute rate expression.

$$\Delta H^* = \Delta H^{\neq} + \boldsymbol{R}T \tag{5}$$

These data are illustrated in Table II.

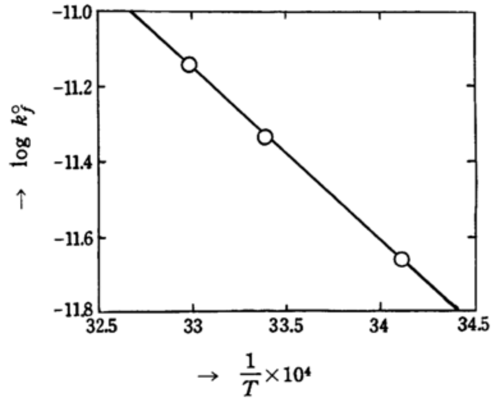

Fig. 2. The temperature dependence of the rate constant of the electrode process of indium(III) in 0.5 F perchlorate.

TABLE II. THE HEAT OF ACTIVATION IN THE ELECTRODE PROCESS OF INDIUM(III) IN 0.5 F PERCHLORATE

The heat of activation at constant pressure ΔH^*, kcal./mol.	The heat of activation at constant volume $\Delta H^{\neq}$, kcal./mol.
21.1	20.5

On applying the absolute rate theory to an electrode process, it is noteworthy that the applied potential plays a role as the activation energy of the electron transfer, and that the electrode reaction is a heterogeneous reaction. It is well known that a spontaneous potential difference exists at the mercury-solution interface. Accordingly, the value of the applied potential as the activation energy must be referred to the zero-charge potential, i. e. the Lippmann-potential. Delahay⁷⁾ has given a modified expression of the absolute rate theory for an electrode reaction which involves no kinetic complication, as is given in Eq. 6, i. e.

$$k_f^\circ = \frac{\boldsymbol{ekT}}{\boldsymbol{h}}\cdot\rho\cdot\exp(-\Delta H^{\neq}/\boldsymbol{R}T)$$
$$\times\exp(\alpha n\boldsymbol{F}E_{\mathrm{m}}/\boldsymbol{R}T)\cdot\exp(\Delta S^{\neq}/\boldsymbol{R}) \tag{6}$$

where e is the transmission coefficient, $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{h}$ is the Planck constant, ρ is an arbitrary factor in cm., E_{m} is the Lippmann potential referred to N. H. E.** and $\Delta S^{\neq}$ is the entropy of activation in e. u. Eq. 6 involves two arbitrary factors. One of them is the transmission coefficient, the value of which was assumed to be 1 in this calculation. The other arbitrary factor is ρ, which was introduced to equalize the dimension of the right side of Eq. 6 to the dimension of the rate constant (cm./sec.).

Delahay has proposed a value as great as that of 2.0×10^{-8} cm. as the mean distance between two depolarizer ions in the bulk solution. It is noteworthy that this value is of the order of the atomic radius. Supposing that the depolarizer at the vicinity of the electrode surface pertains to the rate of the electrode reaction, the above mentioned value of ρ seems to be impossibly small. Accordingly, the value of ρ was evaluated from the depolarizer concentration at the vicinity of the electrode surface. The value amounts to 5.7×10^{-6} cm. as the mean interionic distance between the two depolarizer ions at the vicinity of the electrode surface.

The transmission coefficient does not

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7) P. Delahay, *J. Am. Chem. Soc.*, **75**, 1190 (1953); "New Instrumental Methods in Electrochemistry", Interscience Publishers, Inc. New York (1954), p. 41.

** The Lippmann-potential of the DME in 0.5 F perchlorate was evaluated by the "VDME" method⁸⁾ as great as -0.23_7 V. vs. N. H. E.

8) H. Imai, S. Inouye and S. Chaki, This Bulletin, **31**, 767 (1958); ibid., **32**, 994 (1959).

inherently vary in the order of its magnitude, and accordingly, it does not seriously affect the value of the entropy of activation, while the possible variation of the order of ρ-value seriously affects the value of the entropy of activation. In Table III is presented the value of the entropy of activation evaluated in correspondence to the values of ρ as great as 5.7×10^{-6}.

TABLE III. THE ENTROPY OF ACTIVATION AND THE FREE ENERGY OF ACTIVATION IN THE ELECTRODE PROCESS OF INDIUM(III) IN 0.5 F PERCHLORATE

Arbitrary factor ρ, cm.	Entropy of activation $S^{\neq}$, e. u.	Free energy of activation $F^{\neq}$, kcal.
5.7×10^{-6}	-5.7	22.2

In the above mentioned case the entropy of activation is appreciably negative. Accordingly, it can be assumed that the randomness or disorder in the atomic arrangement of the activated state is less than that of the original state. Lingane[2] has reported that indium(III) is supposed to exist in the form of the aquo complex in the perchlorate solution. Hence, it can be concluded that, when the indium(III) aquo ion enters into the electric field of the electrode surface, the possible coordination of water dipols will be more or less deprived of its randomness prior to the electron transfer.

The reasonable evaluation of ρ-value is reserved for the future.

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