Titrations by Temperature Difference Electrode: Entropy Titrations

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Synopsis. A new type of potential-difference titration which has a relation with the entropy change of a reaction in a titrated solution was demonstrated using a Hg^{2+}–EDTA reaction on an Hg electrode. The potential difference between two identical electrodes, one kept at a different temperature from that of the solution, was monitored during titration. This difference changed from a minimum to a maximum at the equivalent point.

Many titrations concern Gibbs free-energy changes of reactions in titrated solutions. Some titration methods concern only enthalpy changes during reactions. A typical example of titrations concerning Gibbs free-energy changes is a potential-difference titration method in which the potential differences change due to Gibbs free-energy changes, i.e. the equilibrium constants of the reactions during titrations. Therefore, the equilibrium constants which this method concerns must be sufficiently large to determine the equivalent points and the equilibrium constants. In this note, the new type of titration method that is given mainly concerns entropy changes of reactions instead of the equilibrium constants. It is expected to be possible to precisely determine the equivalent points, even though the equilibrium constants are small, and to also calculate the entropy changes using only one titration curve. In ordinary potential-difference (OPD) titrations, entropy changes are calculated from at least two titration curves at different temperatures.

The new method presented here is one type of potential-difference titration in which the potential difference between two identical electrodes (one of which is kept at a different temperature from the titrated solution, called a "temperature difference electrode (TDE)") is monitored during titrations. The temperature of the other electrode is kept equal to that of the solution. In typical cases the potential difference during TDE titration is expected to change sharply from a minimum to a maximum at an equivalent point.[1] A sharp drop in potential was observed at this equivalent point in the case of OPD titration in which the electrode potential was monitored against a reference electrode in an iso-thermal condition. Since the configuration of these two identical electrodes was equal to that of a non-isothermal galvanic cell, their potential difference could be interpreted by the theory of non-isothermal galavanic cells containing a complexation reaction.

A demonstration of TDE titrations was performed using an Hg/Hg^{2+} electrode with disodium dihydrogen ethylenediaminetetraacetate ($EDTAH_2Na_2$) as a ligand for Hg^{2+}. This was done because the potential of Hg/Hg^{2+} is sufficiently stable to measure the small potential difference during TDE titration.

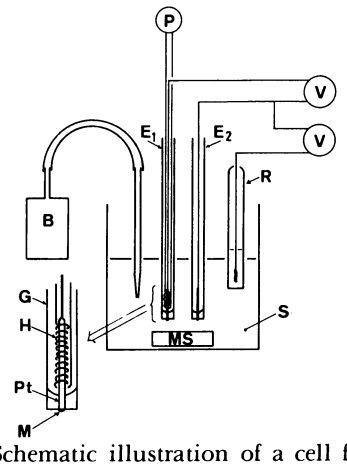

Fig. 1. Schematic illustration of a cell for temperature difference electrode titrations.
B: Motor driven syringe-burette, E_1: temperature difference electrode, E_2: the same type electrode as E_1 without a heater, H: small heater, G: glass tube, M: mercury hanging on Pt, P: power supply for small heater H, Pt: platinum rod, R: reference electrode, S: solution titrated, V: high impedance voltmeter.

Experimental

If a measurement cell for TDE titrations is built well, it will probably be complicated since it must have two compartments at different temperatures and a stirrer which can make all parts of the solution uniform. In this type measurement, the simple cell illustrated in Fig. 1 was used. Two electrodes, consisting of Pt rods (1 mmϕ) on which mercury was hanging, were placed in the cell. One of the electrodes was a TDE in which a small heater of chromel wire (13 Ω) insulated by Teflon was wrapped around the Pt rod in order to make the temperature of the TDE higher than the solution. Since the surface temperature of the TDE was a function of the current passing through this small heater and the speed of the magnetic stirrer, both were kept constant at 150 mA and ca. 150 rpm during titrations. A solution of 50 cm^3 containing $Hg(NO_3)_2$ (0.05 mmol) and sodium nitrate (1 mol dm^{-3}) at pH 1.3 or 2.2 adjusted by nitric acid were titrated by $EDTAH_2Na_2$ solution (0.01 mol dm^{-3}) with a motor-driven syringe-burette (ca. 0.2 $cm^3\,min^{-1}$) of TOA HSM-10A titrator. The cell was placed in a water bath kept at 29°C. The electrochemical system used here is, therefore, written as Hg (29°C)/Hg^{2+}, EDTA, $NaNO_3$/Hg(29°C+ΔT), where 29°C+ΔT is the surface temperature of the mercury of the TDE. The potential difference between two mercury electrodes hanging on the Pt rods and that between the mercury electrode at 29°C and an Ag/AgCl reference electrode which was used in the OPD titrations for comparison were monitored by a computer (HP-9845) with two high-impedance voltmeters (Hokuto HA-104 and ORION 811), a digital voltmeter (HP-3455A), and a scanner (Takeda TR-7216). All measurements were carried out at room temperature (29—30°C).

Results and Discussion

The potential difference measured during the TED

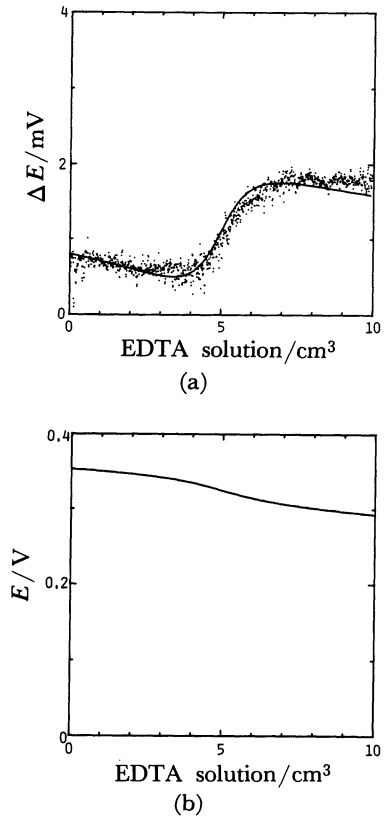

Fig. 2. Titration curves at pH 1.3. (a) by temperature difference electrode. (b) by ordinary potential difference titration.

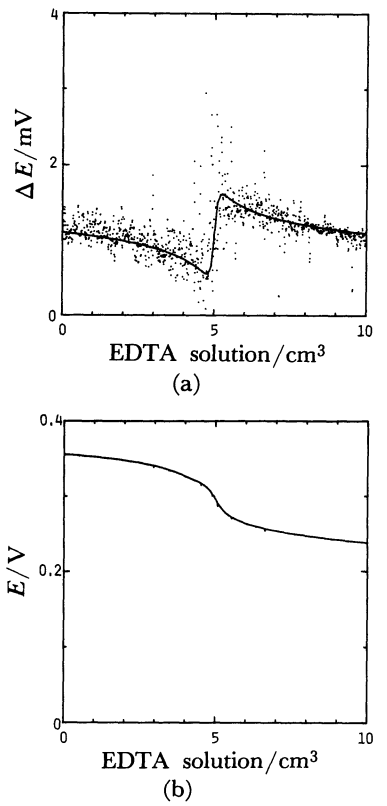

Fig. 3. Titration curves at pH 2.2. (a) by temperature difference electrode. (b) by ordinary potential difference titration.

titrations at pH 1.3 and 2.2 are plotted by dots in Figs. 2(a) and 3(a), and titration curves measured by the OPD ones in the same conditions are shown in Figs. 2(b) and 3(b).

An equivalent point for Hg^{2+} could be determined as the midpoint between the minimum and maximum peaks in the TDE titration curves. At pH 1.3, the equivalent point was determined to be 5.2 cm^3 in titrant volume from the TDE titration curve and 5.0 cm^3 from the OPD one. The difference was nearly within the experimental error. At pH 2.2 it was 5.0 cm^3 for both titration curves. The equivalent points can be seen more clearly in the TDE titration curves than in the OPD curves if measurements are performed under lower noise conditions. From the TDE and OPD titration curves at pH 1.3, regions where the apparent equilibrium constants of the complexation reaction were low, it was confirmed that a sharper change in the potential difference could be observed in case of TDE titration than in the case of OPD titration, even if the equilibrium constant was low. This is because the change in the potential difference during a TDE titration is not only due to the equilibrium constant, but also due to an entropy change of the complexation reaction.

The potential difference (ΔE) observed by the TDE titrations can be expressed by

$$\Delta E = \varepsilon \Delta T,$$

where ε is a thermoelectric power of this system, since two electrodes of the TDE titrations constitute a non-isothermal galvanic cell as described in Experimental. It is well known that the thermoelectric power of a non-isothermal galvanic cell is changed from the initial thermoelectric power (ε_i) at the uniform concentrations just after changing the temperature to the final value after a Soret equilibrium is attained.[2] For the experimental conditions mentioned in this note, the final thermoelectric power might be used for an interpretation of the observed thermoelectric power because of a thin thermal boundary layer on the mercury electrode of the TDE. In this layer, a Soret equilibrium could be attained within a short time. However, the final thermoelectric power in case of cells with a complexation reaction has not been theoretically derived yet. Therefore, in this note the initial thermoelectric power is used for a calculation of the TDE titration curves. This results in only a constant shift in the TDE titration curves since the difference between the initial and final thermoelectric power for general cases is due only to the constant terms of the transport numbers and Eastman entropies.[2] The initial thermoelectric power of the non-isothermal galvanic cells is expressed by the entropy change contributed from the electrode reaction and the transported entropies.[3] When an excess amount of indifferent salts is disolved in the solution, the transported entropies are constant. Therefore, the initial thermoelectric power of a cell $M(T)/M^{n+}$, Ligand/$M(T+\Delta T)$ with an excess amount of the indifferent salts is given as[1]

$$\varepsilon_i = \left(\frac{\partial E}{\partial T}\right)_{\text{iso}} + \text{const.}$$
$$= \frac{R}{nF} \ln C_{M^{n+}} + \frac{RT}{nF}\left(\frac{\partial \ln C_{M^{n+}}}{\partial T}\right) + \frac{\partial E^\circ}{\partial T} + \text{const.}, \quad (1)$$

where R and F are gas and Faraday constants, respectively. $(\partial E/\partial T)_{\text{iso}}$ is the temperature dependence of the isothermal electrode potential (E); i.e., it is determined from the electrode potentials measured against a reference electrode at various temperatures under the condition that the electrode and the reference electrode are kept at the same temperature. The term const. in Eq. 1 arises from transported entropies, activity coefficients, etc., and is constant for an excess of indifferent salts. $C_{M^{n+}}$ is the concentration of free M^{n+} which is not complexed with the ligand. $\partial E^\circ/\partial T$ is the temperature dependence of the standard electrode potential of M/M^{n+}. This term is also constant during titration. Details of the derivation of Eq. 1 is given elsewhere.[1] If the apparent complexation reaction with ligand L is simply written as

$$M^{n+} + L \rightleftarrows M^{n+}L \quad (2)$$

with equilibrium constant K

$$K = \frac{C_{M^{n+}L}}{C_{M^{n+}} C_L}, \quad (3)$$

where $C_{M^{n+}L}$ and C_L are the concentrations of complex $M^{n+}L$, and the free ligand, respectively, $C_{M^{n+}}$ can be calculated from Eq. 3 and the mass balances among them. The first term of Eq. 1 is dependent only on K but the second term of Eq. 1 is dependent on the standard entropy change (ΔS°) of the complexation reaction. Assuming K, ΔS°, and ΔT, it is possible to calculate the TDE and OPD titration curves. From the observed curves K, ΔS°, and ΔT can be determined as follows.

K: By a curve fitting of the OPD titration curve.

ΔT: From a slope of the TDE titration curve between 0 and a half of equivalent point in the titrant volume. In this region the slope of ε_i is not sensitive for K and ΔS° changes.

ΔS°: By a curve fitting of TDE titration curve. It is also possible to determine K from peak shapes in the TDE titration curve. The sharp peak means big K. The peak difference in height is corresponding to ΔS°.

In the above way, K, ΔS°, and ΔT under these experimental conditions were determined to be: log K= 4.9, $\Delta S^\circ = -18$ J K^{-1} mol^{-1}, and ΔT=10 K for pH 1.3 and log K=6.8, $\Delta S^\circ = -25$ J K^{-1} mol^{-1}, and ΔT=5 K for pH 2.2. The differences in ΔT are due to different electrode and stirrer configurations in the cells used. The calculated TDE titration curves are shown by solid lines in Fig. 2(a) and Fig. 3(a).

Since pK of the first proton release reaction of EDTA is 2.0,[4] EDTA forms mainly $EDTAH_4$ at pH 1.3. Therefore, the main complexation reaction at pH 1.3 can be expressed as

$$Hg^{2+} + EDTAH_4 \rightleftarrows HgEDTA^{2-} + 4H^+. \quad (4)$$

From data of stability constants of $EDTAH_4$ and $HgEDTA^{2-}$ found in the literature,[4] apparent $K(=C_{HgEDTA^{2-}}/C_{Hg^{2+}}C_{EDTAH_4})$ and ΔS° in a form of reaction scheme (2) at pH 1.3 are calculated as 6.8 in log K and -40 J K^{-1} mol^{-1}, respectively. The data used here were values at 25 °C and at an ionic strength 1.0 for K and 0.1 for ΔS°. Even though a simple complexation reaction (4) was assumed here, the difference in K and ΔS° between the calculations from values found in the literature and from observed curves was not large. Thus, since it is obvious that TDE titration is related to the entropy change, it might be called "Entropy titration."

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