Measurement of Dissolution Potential Using Rotating Electrodes

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A new cell system consisting of a rotating platinum crystal electrode and rotating reference electrode has been designed for accurate and direct determination of dissolution potentials of electrolytes. The plots of observed dissolution potentials of different electrolytes versus reciprocal of square root of rotation speed are linear and the intercepts yield the values of true dissolution potential when \( \alpha^{0.5} \rightarrow \infty \). The slopes of the linear plots show that diffusion potential is considerably minimised during the measurement.

Dissolution and precipitation potentials of a number of electrolytes have been studied in detail in recent years. New data on precipitation potential using a microelectrode and on dissolution potential using a rotating electrode for a large number of electrolytes have also been studied. Rastogi et al. recently reexamined the theories of precipitation and dissolution potentials and made the model more explicit. In a recent paper a new method of measurement of dissolution potential using a rotating crystal electrode and stationary reference electrode has been described. In this paper measurement of dissolution potential is described using a modified technique where both the electrodes are rotating, thereby eliminating the diffusion potential to a considerable extent at normal rotation speed.

Materials and Methods

The electrolytes NaCl, KCl, KI and CuSO\(_4\).5H\(_2\)O were of AR (BDH) grade and used as such.

Experimental system, shown in Fig. 1, essentially consisted of two rotating platinum electrodes one of which acted as a crystal electrode from where dissolution occurred while the other platinum electrode acted as a reference. The rotation speeds of crystal electrode could be varied and recorded by a speedometer; the reference electrode was rotated at a fixed speed (1500 rpm). The crystal electrode was similar to that described earlier. Measurement of potential was similar to that described earlier. The crystal electrode was loaded with crystals of electrolyte as described in a previous publication. The loaded electrode having a polycrystalline layer of 2mm thickness, was subsequently dried. The crystal and reference electrodes were kept at a distance of 2.5 cm.

The experimental set-up for the measurement of dissolution potential is shown in Fig. 2. The cell system was kept in an ultrathermostat which could control the temperature with an accuracy of \( \pm 0.1^\circ C \). The build-up and decay were automatically recorded with an electronic recorder (Encardio-Rite model 8311) which was calibrated with an electronic voltmeter of input impedance \( \sim 10^{12} \) ohm (Anadigi Digital Electrometer, model OE 5202).

![Figure 1](image_url)

Fig. 1 — Schematic setup of the experimental system. [P = Pyrex tube (ext. diam. = 8 mm, int. diam. = 6 mm, length = 10 cm); H = pyrex tube hole; S = silver ring (int. diam. = 8.2 mm, length = 1 cm); C = carbon brush; W = platinum wire (diam. = 0.45 mm; length = 6 cm); L = iron shaft; Sp = speedometer; Q = metallic plate, K = electrical connection screw; E\(_1\) = reference electrode; and E\(_2\) = crystal electrode]
Fig. 2—Experimental setup for the measurement of dissolution potential [T=thermostat; E<sub>1</sub>=rotating crystal electrode; E<sub>2</sub>=rotating reference electrode; S=silver ring; and R=recorder]

Fig. 3—Plot of \((\Delta \phi)_{diss}\) against \(\omega^{-0.5}\) (where \(\omega\) represents number of rotation per minute of the crystal electrode). [Dotted lines represent the plots when reference electrode was stationary platinum electrode. A,A'=NaCl, B,B'=KCl, C,C'=KI and D,D'=CuSO<sub>4</sub>·5H<sub>2</sub>O]

Results and Discussion

The dissolution potentials of NaCl, KCl, KI and CuSO<sub>4</sub>·5H<sub>2</sub>O using the rotating electrode system at different rotation speeds of crystal electrode and fixed rotation speed (1500 rpm) of reference electrode are plotted in Fig. 3. The values extrapolated for \(\omega^{0.5} \rightarrow \infty\) are recorded in Table 1.

The intercepts of plots in Fig. 3 yield the values of true dissolution potential when \(\omega^{0.5} \rightarrow \infty\). The results are compared with those obtained earlier<sup>5</sup>. Since the diffusion layer thickness<sup>6</sup> is inversely proportional to the square root of \(\omega\), hence slopes show the magnitude of diffusion during the measurements. The slopes of the linear plots in Fig. 3 are smaller than those recorded earlier<sup>5</sup>, indicating that for normal rotation speeds, the diffusion potential developed in the present case has a lower value. However, the intercepts have the same values in each case, showing that the values of absolute dissolution potential obtained by the present set-up agree very well with those observed previously.

Justification of this observation in terms of thermodynamic theory<sup>5</sup> is discussed below. According to thermodynamic theory of Rastogi et al.<sup>5</sup>, \((\Delta \phi)_{diss}\) is given by Eq. (1)

\[
(\Delta \phi)_{diss} = \frac{RT}{F} \left( \frac{U_1^d - U_2^d}{U_1^d + U_2^d} \right) \ln \frac{a^d}{a_{sat}}
\]  

where, \((\Delta \phi)_{diss}\)=dissolution potential, \(F=\)Faraday, \(U_1^d, U_2^d=\)speeds of detachment of cations and anions respectively, \(a^d=\)activity of electrolyte at crystal/solution interface, \(a_{sat}=\)activity of electrolyte in saturated solution, and \(T=\)temperature. The theory has been quantitatively compared with experimental data for alkali halides obtained earlier<sup>5</sup> for which relevant data are available.

It should be noted that speed of detachment of ions is inversely proportional to the ionic radii. Accordingly, we can write as a first approximation

\[
\frac{U_1^d - U_2^d}{U_1^d + U_2^d} \approx \frac{r_2 - r_1}{r_1 + r_2}
\]

where \(r_1, r_2\) represent the ionic radii of cations and anions respectively.

The theory can be qualitatively compared with experimental data as follows. It has been suggested that the sign of \((\Delta \phi)_{diss}\) would be negative if \((U_1^d - U_2^d)/(U_1^d + U_2^d)\) is positive. In other words the potentials would be negative if \(r_2 > r_1\). Results on NaCl, KCl, KI and CuSO<sub>4</sub>·5H<sub>2</sub>O support the hypothesis. The sign of \((\Delta \phi)_{diss}\) for NaCl, KCl, and KI are negative since \((r_2 - r_1)\) is positive whereas the sign is positive for CuSO<sub>4</sub>·5H<sub>2</sub>O since \((r_2 - r_1)\) is negative.

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References