

Experimental Study of the Moving Chemical Reaction Boundary Formed by Co^{2+} and OH^-

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Cao, C.-X. and Chen, W.-K., 1998. Experimental Study of the Moving Chemical Reaction Boundary Formed by Co^{2+} and OH^- . – Acta Chem. Scand. 52: 714–717. © Acta Chemica Scandinavica 1998.

Experiments on the moving chemical reaction boundary (MCRB) formed by Co^{2+} and OH^- have been performed in 1% (w/v = weight/volume) agarose gel containing 0.1 N background electrolyte KCl. The results show that the MCRB experiments are quantitatively in agreement with the predictions of the MCRB theory. Thus, the experiments directly demonstrate the correctness of the theory.

1. Introduction

In our previous reports^{1–3} the concept of a moving chemical reaction boundary (MCRB) was proposed, the MCRB theory was advanced and a series of moving chemical reaction boundary equations (MCRBEs) were formulated. From the MCRBEs, one can get

$$\mu^{\alpha\beta} = \frac{m_+^\alpha c_+^\alpha E^\alpha - m_-^\beta c_-^\beta E^\beta}{c_+^\alpha - c_-^\beta} \quad (1)$$

where the superscripts α and β indicate phase α and β , respectively, the subscripts $+$ and $-$ indicate positive and negative reacting ions like Co^{2+} and OH^- , respectively, m is the mobility, c the equivalent concentration, and E the electric strength. Here m and c are positive if the ion carries net positive charge(s) or negative if net negative charge(s), as defined by Dole,⁴ Alberty⁵ and one of the authors.^{2,3}

The theory of the MCRB has been partly proved by the experiments by Deman and Rigole^{6,7} and by Pospichal *et al.*,⁸ and computer simulations based upon Kohlrausch's *beharrliche* function.^{1,8}

However, systematic experiments have not been performed up to now. Thus the purpose of work reported here is to test the validity of MCRBEs with the experiments of MCRB formed by positive and negative reacting ions, Co^{2+} and OH^- .

2. Experimental procedures

The reagents used here were $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NaOH and KCl, all of them of AR grade (Shanghai Chemical Reagent Co., Shanghai, China). The agarose used to

prepare the gel was a biochemical reagent (Shanghai Huang-Hua Pharmaceutical Factory, Shanghai, China). Agarose gel, produced from agar, is preferred in contrast to agar gel, since in agarose gel there is nearly complete absence of electro-osmotic flow (EOF), but the agar has EOF, due to the existence of charged groups in agar gel.⁹

A power supply (DYYIII8A, Beijing Luyi Instrument Factory, Beijing, China), with constant voltage 0–150 or 0–600 V, constant current 0–25 or 0–100 mA and timer equipment, is used to yield direct current. A disc electrophoretic trough (DYYIII27, Beijing Luyi Instrument Factory), together with electrophoretic tubes, is used to perform the MCRB formed by Co^{2+} and OH^- .

The MCRB experiments were mainly carried out according to the procedures given in Refs. 6 and 7, but with some modifications.

As shown in Fig. 1a, for the anodic movement of MCRB, initially phase α contains 1% (w/v = weight/volume) agarose gel in tube (but no gel in the anodic vessel), 0.1 N background electrolyte KCl and 0.004–0.02 N, viz. 4–20 equiv. m^{-3} CoCl_2 , and phase β , viz. the cathode vessel, holds 0.1 N KCl and 0.001–0.02 N, viz. 1–20 equiv. m^{-3} NaOH.

As shown in Fig. 1b for the cathodic movement of MCRB, at the beginning, phase α , viz. the anodic vessel, contains 0.1 N KCl and 0.04/or 0.014 N CoCl_2 , and phase β holds 1% (w/v) agarose gel in the tube (but no gel in the cathodic trough), 0.1 N KCl and 0.001/or 0.002 N NaOH.

Each run includes two tubes which are filled with 1% (w/v) agarose gel containing 0.1 N KCl and 0.004–0.014 N CoCl_2 (Fig. 1a), or 0.001–0.02 N NaOH (Fig. 1b).

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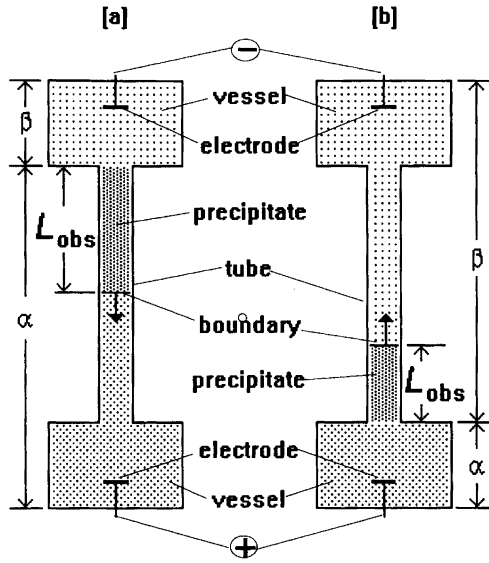


Fig. 1. The experimental procedures of MCRB. [a] shows the procedure for the anodic movement of the boundary; [b] means the procedure for the cathodic movement of the boundary. + and - imply the anode and cathode, respectively; the arrows, ↓ and ↑, in tubes indicate the direction of boundary movement. For other symbols see the text.

During each run with two tubes, the blue precipitate reaction boundary, viz. the ‘precipitate reaction front’ as called by Deman and Regole,^{6,7} is formed and moves toward the anode or cathode; the precipitate zone is developed just after the boundary. After each run, the displacements of boundaries for the two tubes (L_{obs} ; the positive and negative mean the cathodic and anodic movements, respectively) are equal to the lengths of precipitate zones, which can be directly determined with a vernier caliper; the observed velocity ($\mu_{\text{obs}}^{\alpha\beta}$; the positive and negative mean the cathodic and anodic movements, respectively) can directly be calculated by

$$\mu_{\text{obs}}^{\alpha\beta} = \bar{L}_{\text{obs}}/t_{\text{obs}} \quad (2a)$$

$$\bar{L}_{\text{obs}} = \frac{1}{2}(L_{1,\text{obs}} + L_{2,\text{obs}}) \quad (\text{due to each run with two tubes}) \quad (2b)$$

where t_{obs} , the run time, is equal to 10 min, viz. 600 s, for each run.

Owing to the existence of background electrolyte KCl in a large quantity, the conductivity is considered to be uniform over a whole conductor⁶⁻⁸ (the conductivity of solution containing 0.1 N KCl and 0.01 N CoCl_2 /or NaOH is equal to 1.22 S m^{-1} at 25°C), viz.

$$E^\alpha = E^\beta \quad (3a)$$

or

$$I/q\kappa^\alpha = I/q\kappa^\beta \quad (3b)$$

During the 10 min run, the electric current, I (in A), as shown in Fig. 2, is recorded, the mean electric current,

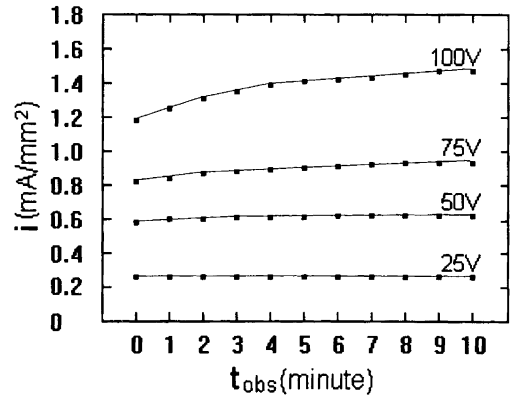


Fig. 2. Variation of the current intensity with time to 10 min at the voltages 25, 50, 75 and 100 V. The runs are according to the procedure in Fig. 1a. Conditions: phase α containing 0.01 N CoCl_2 and 0.1 N KCl; phase β containing 0.01 N NaOH and 0.1 N KCl; I.D. of tube 5.8 mm, length 90 mm; run time 10 min; each run with two tubes.

\bar{I} , is calculated from

$$\bar{I} = \sum_{i=0}^{10} I_i/11 \quad (i = 0, 1, 2, \dots, 10 \text{ min}) \quad (4)$$

and the mean electric current intensity (\bar{i} , in A m^{-2}) is computed by

$$\bar{i} = \bar{I}/2q \quad (\text{due to each run with two tubes}) \quad (5)$$

For the existence of high ionic strength, the mobilities of Co^{2+} and OH^- in eqn. (1) should be corrected by the empirical equation given by the author^{10,11}

$$m_{\text{act}} = m_0 \exp(-\eta\sqrt{zI}) \quad (\eta = 0.77 \text{ if } z \geq 2; \eta = 0.50 \text{ if } z = 1) \quad (6)$$

where m_{act} and m_0 are the actual and absolute mobilities, respectively, $I(=0.5\sum cz_i^2)$ is the ionic strength, z the ionic valence, and η the coefficient. Note here, the overall/or apparent mobilities of Co^{2+} and OH^- are equal to their actual mobilities owing to the complete ionization of the strong reaction electrolytes CoCl_2 and NaOH and the absence of EOF in agarose gel (Ref. 9, pp. 106 and 137).

The absolute mobility of hydroxide ion, m_{0,OH^-} , obtained from Ref. 12, is $20.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the absolute mobility of $m_{0,\text{Co}^{2+}}$ ($=5.7 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) is calculated from the equivalent conductivity ($\lambda_0 = 5.5 \times 10^{-3} \text{ m}^2 \text{ S mol}^{-1}$) of Co^{2+} in infinite diluted solution¹³ with $m_0 = \lambda_0/F$ (F is the Faraday constant).

For the reasons mentioned above, in this paper the theoretic velocity of the boundary should be calculated with eqn. (7), which is obtained from the insertions of eqns. (3)–(6) into eqn. (1):

$$\mu_{\text{the}}^{\alpha\beta} = \frac{m_{\text{act},\text{Co}^{2+}}^\alpha c_{\text{Co}^{2+}}^\alpha - m_{\text{act},\text{OH}^-}^\beta c_{\text{OH}^-}^\beta}{(c_{\text{Co}^{2+}}^\alpha - c_{\text{OH}^-}^\beta)\kappa} \quad (7)$$

In order to avoid the effect of proton and hydroxide ion produced in electrolysis on this run and on the next run, the run time should be short (e.g. 10 min), and a

new analyte and catholyte, each in 400 ml, should be used for each run.

3. Results and discussion

In order to achieve an optimum experimental conditions, we performed a series of experiments at different constant voltage. As shown in Fig. 2, at high voltage, such as 100 V, the electric current intensity alters with time obviously, whereas at low voltage, e.g. 25 V, the intensity is constant with time but the precipitate zone is short. Thus, in most runs, we use a constant voltage of 50 V, under which the intensity is almost constant with time and the precipitate zone is longer in contrast to that for 25 V.

As shown in Fig. 3, even when the concentrations of Co^{2+} and OH^- , $c_{\text{Co}^{2+}}^{\alpha}$ and $c_{\text{OH}^-}^{\beta}$ ($c_{\text{Co}^{2+}}^{\alpha} = c_{\text{OH}^-}^{\beta}$ is set here), alter from 0.004 to 0.008 and to 0.014 N, the current intensities are almost constant among different runs. This directly shows the validity of the background electrolyte KCl to create a uniform and constant current intensity [equivalently, electric field strength, see eqn. (3)] over a whole conductor.

According to eqn. (7), the velocity of the boundary is proportional to the current intensity. Thus the higher the intensity \bar{i} , the faster the velocity. This prediction is, as shown in Fig. 4, in agreement with the experiments of MCRB. It is revealed that the correlation coefficient (CC) is equal to 0.9984 ($n=8$).

As shown in eqn. (7), if one increases the concentrations of Co^{2+} and OH^- , $c_{\text{Co}^{2+}}^{\alpha}$ and $c_{\text{OH}^-}^{\beta}$, synchronously and keeps other conditions constant, one can achieve a constant boundary velocity. This prediction is proved by the experiments in Fig. 5, which show that the boundary velocities for the five runs are almost completely constant. It is calculated that the CC between $\mu_{\text{obs}}^{\alpha\beta}$ and $\mu_{\text{the}}^{\alpha\beta}$ is 0.9895 ($n=5$).

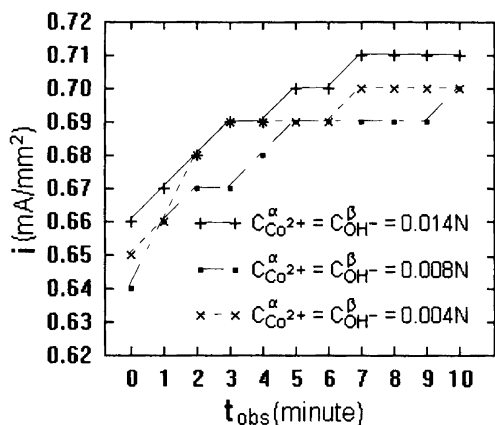


Fig. 3. Variation of the current intensity with time to 10 min at different concentrations of reaction ions. The runs are according to the procedure in Fig. 1a. Conditions: voltage 50 V; phase α containing 0.004, 0.008 or 0.014 N CoCl_2 and 0.10 N KCl, and phase β containing 0.004, 0.008 or 0.014 N NaOH and 0.10 N KCl; I.D. of tube 4.0 mm, length 90 mm; run time 10 min; each run with two tubes.

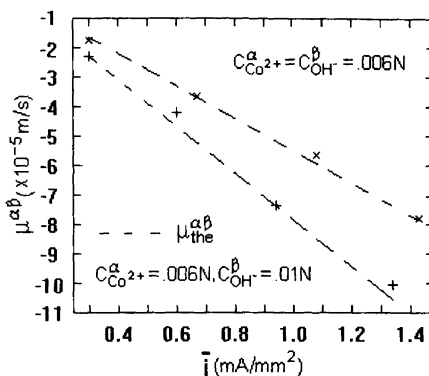


Fig. 4. Variation of the boundary velocity with electric current intensity. The procedure and conditions are the same as those in Fig. 2.

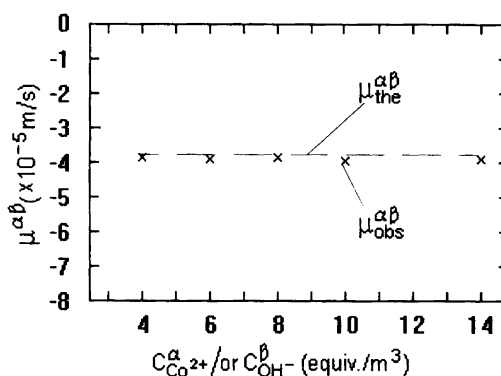


Fig. 5. Boundary velocities at different concentrations of $c_{\text{Co}^{2+}}^{\alpha}$ or $c_{\text{OH}^-}^{\beta}$ ($c_{\text{Co}^{2+}}^{\alpha} = c_{\text{OH}^-}^{\beta}$ is set here). The runs are according to the procedure in Fig. 1a. Conditions: 50 V; phase α containing 0.004–0.014 N, viz. 4–14 equiv./ m^3 CoCl_2 and 0.1 N KCl, and phase β containing 0.004–0.014 N NaOH and 0.1 N KCl; I.D. of tube 4.0 mm, length 90 mm; run time 10 min; each run with two tubes.

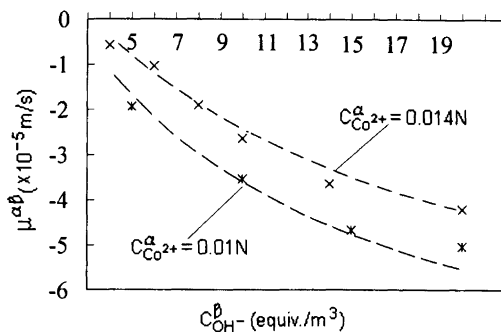


Fig. 6. Boundary velocity at different values of $c_{\text{OH}^-}^{\beta}$ ($c_{\text{Co}^{2+}}^{\alpha}$ is fixed at 0.01 or 0.014 N). The runs are according to the procedure in Fig. 1a for velocity less than zero, or in Fig. 1b for velocity greater than zero. Conditions: 50 V; phase α containing 0.01 or 0.014 N CoCl_2 and 0.1 N KCl, and phase β containing 0.001–0.02 N NaOH and 0.1 N KCl; I.D. 4.6 mm; run time 10 min; each run with two tubes.

Equation (7) indicates that, if $c_{\text{Co}^{2+}}^{\alpha}$ is fixed, an increase in $c_{\text{OH}^-}^{\beta}$ leads to a decrease in the velocity of the boundary, whereas the curve between $\mu^{\alpha\beta}$ and $c_{\text{OH}^-}^{\beta}$ is not linear but a reverse curve. This prediction with eqn. (7) is verified

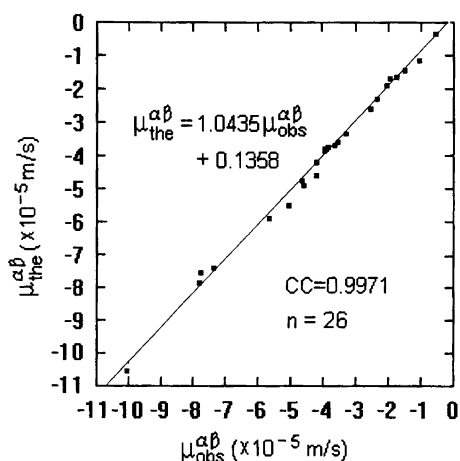


Fig. 7. The correlations between $\mu_{\text{the}}^{\alpha\beta}$ and $\mu_{\text{obs}}^{\alpha\beta}$ ($n=26$).

by the experiments in Fig. 6. An excellent correlation exists between $\mu_{\text{obs}}^{\alpha\beta}$ and $\mu_{\text{the}}^{\alpha\beta}$ ($CC=0.9952$, $n=9$). It is also found that no (or a very weak) precipitate zone exists if the concentration of hydroxide ion, $c_{\text{OH}^-}^{\beta}$, is less than 0.004 N, e.g. 0.002 and 0.001 N, as performed by us with the procedure in Fig. 1b.

After all of 26 runs are completed, the correlations between $\mu_{\text{obs}}^{\alpha\beta}$ and $\mu_{\text{the}}^{\alpha\beta}$ are analysed. As shown in Fig. 7, the value of CC is 0.9971 ($n=26$), the linear regression equation is $\mu_{\text{the}}^{\alpha\beta} = 1.0435\mu_{\text{obs}}^{\alpha\beta} + 0.1358$, which is approximately equivalent to $\mu_{\text{obs}}^{\alpha\beta} = \mu_{\text{the}}^{\alpha\beta}$. This proves the validity of eqns. (1) and (7) further.

It is clear from the results above that the predictions of eqns. (1) and (7) are quantitatively in agreement with the experiments of MCRB, and an excellent relationship exists between the theoretical and observed velocities, viz. $\mu_{\text{obs}}^{\alpha\beta}$ and $\mu_{\text{the}}^{\alpha\beta}$. Thus, some of the MCRBEs are directly verified by experiment.

Acknowledgements. This work was supported partly by the National Natural Scientific Foundation of China (approved no. 29775014), partly by the Education Board of Anhui Province (approved no. 97TL465), and partly by Wannan Medical College.

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Received August 19, 1997.