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Short communication

Corrections to moving chemical reaction boundary equation for weak reactive electrolytes under the existence of background electrolyte KCl in large concentrations

Cheng-Xi Cao^{a,*}, Shu-Lin Zhou^{a,b}, You-Zhao He^a, Yi-Tai Qian^a, Li Yang^a, Qi-Shu Qu^a,
Wu-Er Gan^a, Lin Dong^a, Yao-Qiang Zhao^a, Wen-Kui Chen^b

^aDepartment of Chemistry, University of Science and Technology of China, 230026 Hefei, China

^bInstitute of Allergy Reaction, Wannan Medical College, 241001 Wuhu, China

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Abstract

In this report, the moving chemical reaction boundary (MCRB) was formed by the weak reaction electrolytes of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of background electrolyte KCl in large concentrations, the experiments were compared with the predictions by the moving chemical reaction boundary equation (MCRBE) for weak reactive electrolytes. It was found that the experimental results are far from the predictions with the MCRBE. So the MCRBEs must be corrected under the given experimental conditions. The corrected MCRBEs are given for the MCRB formed with weak reactive electrolytes coupled with KCl at high concentrations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The theory of the moving chemical reaction boundary (MCRB) has been gradually developed by Deman and Rigole [1,2], Pospichol et al. [3] and Cao et al. [4–7]. The theory possesses important uses in classic isoelectric focusing (IEF) [8–12] as demonstrated by Cao [13–15], in the preparation of colloids and in nano-particle materials as also shown by Cao et al. [16,17].

The theory of the MCRB has been partially proved by some experiments. The experiment of moving precipitate reaction boundary (MPRB), viz. “precipitate reactive front” as termed by Deman and Rigole [1,2], proved the concept of MCRB qualitatively. The experiments of electrically controlled electrofocusing by Pospichol and co-workers [3,18,19] were quantitatively in agreement with the prediction by the stationary neutralization reaction boundary equation (SNRBE) deduced from the moving chemical reaction boundary equation (MCRBE) [5,13]. The experiments of MPRB formed with cobaltic and hydroxyl ions by Cao and co-workers [20,21] demonstrated the theory of the MCRB exactly and systemically. The recent results of the moving neu-

*Corresponding author. Tel.: +86-551-360-1589; fax: +86-551-363-1760.

E-mail addresses: cxcao@mail.ustc.edu.cn (C.-X. Cao), yqtqian@ustc.edu.cn (Y.-T. Qian).

tralization reactive boundary (MNRB) formed by strong acid and alkali further manifested the theory quantitatively [22,23].

If an MNRB is formed by weak acid and alkali under the existence of background electrolyte KCl in large concentrations, it was found, however, that the MCRBE cannot predict the movement of the MNRB. Here our purposes are to test and correct the MCRBE for both the anodic and cathodic movement of the boundary formed with weak reactive electrolytes (such as $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH discussed here) under the existence of KCl in large concentrations, but not to use the theory for application purposes.

2. Experimental

The reagents used here are $\text{NH}_3 \cdot \text{H}_2\text{O}$, CH_3COOH , KCl, bromophenol blue and agarose, the former three are analytical grade (AG) (purchased from Shanghai Chemical Reagents, Shanghai, China), bromophenol is a chemical grade (CG) (purchased from Shanghai Chemical Reagents), and agarose is biochemical reagent grade (purchased from Shanghai Huang-Hua Pharmaceutical Factory, Shanghai, China).

A laboratory-made apparatus is used for the experiments of MNRB formed with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH . The procedure is according to the “electrolytic-continuous-flow-moving chemical reaction boundary method” (ECF-MCRBM) described in Refs. [21,22]. For better understanding, Fig. 1 shows the diagrams of two kinds of ECF-MCRBM, one moving towards to the anode (see Fig. 1A) and another towards the cathode (see Fig. 1B). The neutralization reaction of electromigration occurs in the 1% agarose gel in the tube. The experimental results of the MNRBs formed with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH are shown in Figs. 2 and 3, and in Tables 1 and 2.

In the anodic movement of the MNRBs shown in Figs. 1A and 2, phase α contains 0.1 M KCl and 0.008–0.02 M CH_3COOH and phase β contains 0.1 M KCl and 0.8 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. In the cathodic movement of the MNRBs displayed in Figs. 1B and 3, phase α contains 0.1 M KCl and 0.6 M CH_3COOH and phase β contains 0.1 M KCl and 0.004–0.016 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. In both the anodic and

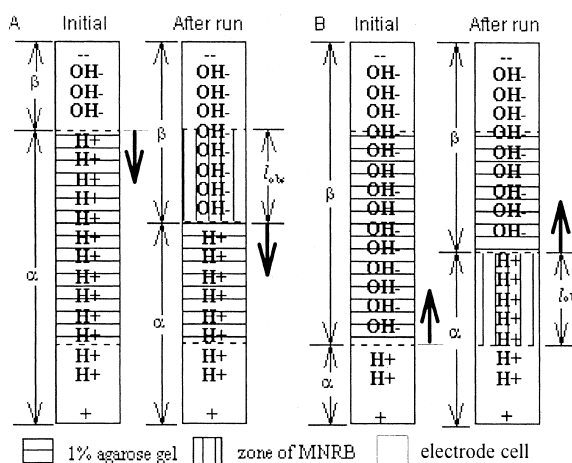


Fig. 1. The diagrams of the MCRBMs formed with acid and alkali. (A) The anodic movement of the boundary; (B) the cathodic movement of the boundary. Phase α contains the weak acid of CH_3COOH and 0.1 M background electrolyte KCl, phase β contains the weak alkali of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 0.1 M KCl. + and – indicate the anode and cathode, respectively, the hard arrows imply the moving direction of MNRB. For other symbols see the text.

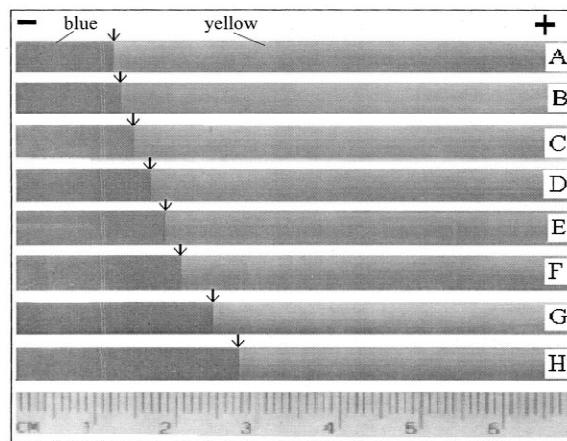


Fig. 2. The 10-min anodic movements of the MCRB created with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of 0.1 M background electrolyte KCl in 1% gel. Conditions: phase α containing 0.1 M KCl+ (A) 0.02 M, /or (B) 0.018 M, /or (C) 0.016 M, /or (D) 0.014 M, /or (E) 0.012 M, /or (F) 0.01 M, /or (G) 0.008 M, /or (H) 0.006 M CH_3COOH ; phase β having 0.1 M KCl+0.8 M $\text{NH}_3 \cdot \text{H}_2\text{O}$; 1% agarose gel; 0.1% bromophenol blue; current intensity=0.6 mA/mm²; run time=10 min; I.D. of tube=4.4–5.0 mm; length of tube=90 mm; flow-rate of anolyte and catholyte=0.6 ml/min. The method is according to Fig. 1A. The anode is on the right and the cathode on the left.

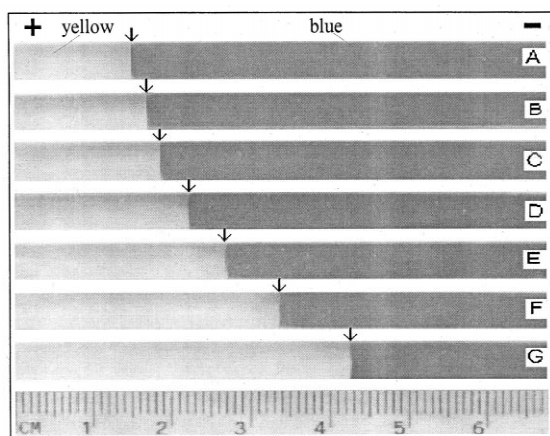


Fig. 3. The 10-min cathodic movements of the MCRB created with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of 0.1 M background electrolyte KCl in 1% gel. Conditions: phase β containing 0.1 M KCl+ (A) 0.016 M, /or (B) 0.014 M, /or (C) 0.012 M, /or (D) 0.010 M, /or (E) 0.008 M, /or (F) 0.006 M, /or (G) 0.004 M $\text{NH}_3 \cdot \text{H}_2\text{O}$; phase α having 0.1 M KCl+0.8 M CH_3COOH ; 1% agarose gel; 0.1% bromophenol blue; current intensity = 0.6 mA/mm²; run time = 10 min; I.D. of tube = 4.4–5.0 mm; length of tube = 90 mm; flow-rate of anolyte and catholyte = 0.6 ml/min. The method is according to Fig. 1B. The anode is on the left and the cathode on the right.

cathodic moving experiments, the 1% agarose gel is used as an anti-convection medium, and 0.1% bromophenol blue in the gel is used as a marker that denotes the yellow acidic and blue alkaline zones and the boundary.

The original theoretical computation of the MCRB formed with the weak reactive electrolytes of

$\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH relied upon the following boundary velocity equation:

$$\mu_{\text{weak}}^{\alpha\beta} = \frac{\bar{m}_+^{\alpha} \bar{c}_+^{\alpha} E^{\alpha} - \bar{m}_-^{\beta} \bar{c}_-^{\beta} E^{\beta}}{\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}} = i \frac{\left(\frac{\bar{m}_+^{\alpha} \bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta} \bar{c}_-^{\beta}}{\kappa^{\beta}} \right)}{(\bar{c}_+^{\alpha} - \bar{c}_-^{\beta})} \quad (1)$$

which is transformed from the MCRBE for weak reactive electrolyte:

$$\frac{\bar{m}_+^{\alpha} \bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta} \bar{c}_-^{\beta}}{\kappa^{\beta}} = v^{\alpha\beta} (\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}) \quad (2)$$

in Eqs. (1) and (2), $\mu_{\text{weak}}^{\alpha\beta}$ is the velocity of boundary $\alpha\beta$ formed by weak reactive electrolytes; m and c are, respectively, the electrophoretic mobility and concentration, the bar over them means the “constituent mobility” and “constituent concentration”, respectively, the subscripts + and – imply the positive and negative reactive ions, such as H^+ and OH^- , respectively, the superscripts α and β indicate phase α and β , respectively; κ is the specific conductivity of a phase (here, $\kappa^{\alpha} = \kappa^{\beta} = 1.29$ S/m at 25°C, due to the very high concentration of KCl, as have been reported by Deman and Rigole [1,2], Pospichol et al. [3] and Cao and co-workers [20–23]); i the current intensity, $v^{\alpha\beta}$ the boundary displacement per-Coulomb electric charge.

In Eqs. (1) and (2), there exist [24]:

$$\bar{m}_+^{\alpha} \bar{c}_+^{\alpha} = m_+^{\alpha} c_+^{\alpha} \quad (3)$$

Table 1

The observed, original theoretical and corrected theoretical velocities of the anodic moving MCRB created with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of 0.1 M background electrolyte KCl in 1% agarose gel^a

	Label ^b							
	A	B	C	D	E	F	G	H
Phase $\alpha = 0.1$ M KCl + [CH_3COOH] (M)	0.02	0.018	0.016	0.014	0.012	0.010	0.008	0.006
Phase $\beta = 0.1$ M KCl + [$\text{NH}_3 \cdot \text{H}_2\text{O}$] (M)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
μ_{obs} ($\cdot 10^{-5}$ m/s)	-2.00	-2.25	-2.38	-2.83	-3.00	-3.38	-4.00	-4.75
μ_{ori} (Eq. (1)) ($\cdot 10^{-5}$ m/s)	-0.067	-0.068	-0.068	-0.069	-0.070	-0.071	-0.072	-0.073
$\mu_{\text{obs}}/\mu_{\text{ori}}$	29.85	33.09	35.00	41.01	42.85	47.61	55.56	65.07
μ_{cor} (Eq. (8)) ($\cdot 10^{-5}$ m/s)	-2.02	-2.20	-2.41	-2.66	-2.97	-3.36	-3.85	-4.49
$\mu_{\text{obs}}/\mu_{\text{cor}}$	0.99	1.02	0.99	1.06	1.01	1.01	1.04	1.06

^a The experiments are the same as those in Fig. 2.

^b The labels are correspondent to those in Fig. 2.

Table 2

The observed, original theoretical and corrected theoretical velocities of the cathodic moving MCRB created with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of 0.1 M background electrolyte KCl in 1% agarose gel^a

	Label ^b						
	A	B	C	D	E	F	G
Phase $\alpha=0.1$ M KCl + $[\text{CH}_3\text{COOH}]$ (M)	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Phase $\beta=0.1$ M KCl + $[\text{NH}_3 \cdot \text{H}_2\text{O}]$ (M)	0.016	0.014	0.012	0.010	0.008	0.006	0.004
μ_{obs} ($\cdot 10^{-5}$ m/s)	2.50	2.83	3.21	3.71	4.42	5.46	7.04
μ_{ori} ($\cdot 10^{-5}$ m/s) (Eq. (1))	0.069	0.070	0.072	0.073	0.074	0.076	0.078
$\mu_{\text{obs}}/\mu_{\text{ori}}$	36.23	40.43	44.58	50.82	59.73	71.84	90.26
μ_{cor} ($\cdot 10^{-5}$ m/s) (Eq. (8))	2.21	2.50	2.87	3.36	4.02	4.99	6.51
$\mu_{\text{obs}}/\mu_{\text{cor}}$	1.13	1.13	1.12	1.11	1.10	1.09	1.08

^a The experiments are the same as those in Fig. 3.

^b The labels are correspondent to those in Fig. 3.

$$\bar{m}^{\beta} \bar{c}^{\beta} = m^{\beta} c^{\beta} \quad (4)$$

The ionic mobilities in Eqs. (1)–(4) should be corrected with the empirical equation:

$$m_{\text{act}} = m_0 \exp(-0.5\sqrt{\eta l}) \quad (5)$$

$$I = 0.5 \sum_i c_i z_i^2 \quad (6)$$

which is of validity for large organic ions with low electric charge intensities [25–27] and small inorganic ions with high electric charge intensities [28,29], if ionic strength is not greater than 0.1 M. The absolute mobilities of H^+ and OH^- at 25°C, cited from Ref. [30], are, respectively, 36.3 and $20.5 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

All of the experimental data treatments and the theoretical computation were performed with the software Microcal Origin (ver. 5.0; Microcal, USA).

3. Results and discussion

According to the ECF-MCRBM described in Fig. 1A, a series of experiments of MCRB created by $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH were performed under high concentrations of KCl. The results are shown in Fig. 2, in which the length (l_{obs}) of movement of the MCRB (which is the length of the blue zone from the cathode end to the mark arrows) can be directly monitored. The observed velocity (μ_{obs}) can be calculated with:

$$\mu_{\text{obs}} = l_{\text{obs}}/t \quad (7)$$

where, t is the time (s). The observed velocities of boundary in Fig. 2 are given in Table 1. The alphabets of Table 1 are correspondent to those in Fig. 2.

The original theoretical values of the anodic moving MNRB computed by Eq. (1) for the experiments of Fig. 2 are also displayed in Table 1.

Table 1 shows the experimental and theoretical results of anodic movement of MNRB formed by weak reactive electrolytes $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH together with the background electrolyte KCl at high concentration. In Table 1, comparing the original theoretical velocities computed by Eq. (1) with the observed velocities by Eq. (7), one can obviously find a great difference between the observed and original theoretical velocities: the ratio between the observed and original theoretical velocities ranges from 30 to 65. The results imply very strong discrepancy between the observed and original theoretical velocities computed by Eq. (1), if the MNRB is formed by weak acid and alkali under the existence of a high concentration of KCl and the theoretical velocity is computed with Eq. (1). Therefore, Eq. (1), including Eq. (2), possesses no validity for the MNRB formed with weak acid and alkali under high concentration of KCl, the MNRBE, viz. Eqs. (1) and (2), must be corrected.

The corrected MNRBEs are given as Eqs. (8) and (9), which are for the anodic movement of the MNRB formed by weak acid and alkali, coupled with the background electrolyte KCl at high concentrations:

$$\mu_{\text{weak}}^{\alpha\beta} = \frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}E^{\alpha} - \bar{m}_-^{\beta}\bar{c}_-^{\beta}E^{\beta}}{\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}} = i \frac{\left(\frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta}\bar{c}_-^{\beta}}{\kappa^{\beta}}\right)}{(\bar{c}_+^{\alpha} - \bar{c}_-^{\beta})} \quad (8)$$

which was transferred from the MCRBE for the weak reactive electrolyte:

$$\frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta}\bar{c}_-^{\beta}}{\kappa^{\beta}} = v^{\alpha\beta}(\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}) \quad (9)$$

The corrected theoretical results calculated with Eq. (8) for the experiments of Fig. 2 are also collected in Table 1. As shown in Table 1, the ratio of the observed and corrected theoretical velocities by Eq. (8) are all near to one, this means that there is a good agreement between the observed velocity and the corrected theoretical velocity by Eq. (8). Therefore, Eq. (8), together with Eq. (9), is valid for the experiments of anodic movement MNRBs formed by weak reactive electrolytes $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH , coupled with the high concentration of KCl.

Fig. 3 and Table 2 show the experimental and theoretical results of cathodic movement of the MNRB formed by the weak reactive electrolytes $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH coupled with the high concentration of background electrolyte KCl. As given in Table 2, the ratio of the observed and original theoretical values computed with Eq. (1) change from 36 to 90, very high values of the ratio, the ratio also demonstrates that the observed velocities of the MNRB are clearly in disagreement with the original theoretical values computed by Eq. (1). Hence, Eq. (1) also holds no validity for the cathodic movement of the MNRB formed by the weak reactive electrolytes $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CH_3COOH under the existence of high concentration of KCl. Under the experimental conditions of Fig. 3, Eqs. (1) and (2) should be corrected as, respectively:

$$\mu_{\text{weak}}^{\alpha\beta} = \frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}E^{\alpha} - \bar{m}_-^{\beta}\bar{c}_-^{\beta}E^{\beta}}{\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}} = i \frac{\left(\frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta}\bar{c}_-^{\beta}}{\kappa^{\beta}}\right)}{(\bar{c}_+^{\alpha} - \bar{c}_-^{\beta})} \quad (10)$$

$$\frac{\bar{m}_+^{\alpha}\bar{c}_+^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_-^{\beta}\bar{c}_-^{\beta}}{\kappa^{\beta}} = v^{\alpha\beta}(\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}) \quad (11)$$

The corrected theoretical velocities by Eq. (10) for the experiments in Fig. 2 are also given in Table 2. As shown in Table 2, a good coincidence exists between the observed velocities of Fig. 2 and the corrected theoretical velocities by Eq. (10), this directly shows the validity of the corrected Eq. (10) for the experiments of the MNRB in Fig. 2.

4. Conclusions

From the above results and discussion, it is evident that, the MCRBE, viz. Eqs. (1) and (2), hold no validity for both the anodic and the cathodic movement of the MNRB formed by weak reactive electrolytes coupled with the high concentration KCl, and Eqs. (1) and (2) should be corrected as Eqs. (8) and (9), respectively, if the boundary is an anodic movement of the MNRB, and should be corrected as Eqs. (10) and (11), respectively, if a cathodic movement of the MNRB.

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