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# Experimental investigation on moving chemical reaction boundary theory for weak-acid–strong-base system with background electrolyte KCl in large concentration

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## Abstract

In this report, the moving chemical reaction boundary (MCRB) was formed with the weak acid of acetic acid (HAc) and the strong alkali of NaOH, coupled with the excess of background electrolyte KCl. The experiments were compared with the predictions by the moving chemical reaction boundary equation (MCRBE). It is very interesting that (1) the experimental results are in good agreement with the predictions with the original MCRBE if the MCRB is an anodic moving boundary, (2) however, the experiments are extremely far away from the predictions with the original MCRBE if a cathodic moving boundary. Hence, the original MCRBE must be corrected under the later situation of cathodic moving MCRB. The corrected MCRBE was well quantitatively proved to be valid for the cathodic moving MNRB formed with the same electrolytes of HAc, NaOH and KCl. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Moving chemical reaction boundary; Isoelectric focusing; Acetic acid; Sodium hydroxide

## 1. Introduction

The theory of moving chemical reaction boundary (MCRB) has been developed gradually. In 1970, Deman and Rigole [1,2] firstly advanced the important idea of “precipitate reactive front” — the original of the MCRB concept, and in their theory, they conceived the key important relation — the

equilibrium of equivalent numbers of positive and negative reaction ion in a MCRB system. In 1993, Pospichol et al. [3] developed the concept of stationary neutralization reaction boundary (SNRB), together with the equation of SNRB, holding clear significance of electro-focusing in capillary electrophoresis (CE). In 1997–1999, we [4–7] formally evolved the concept of MCRB, developed the theory of MCRB, deduced the moving chemical reaction boundary equation (MCRBE), coupled with stationary chemical reaction boundary equation (SCRBE) and judgement expression.

The theory of MCRB, including its relative ex-

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perimental method, has some significant application in chemistry. Deman and Rigole [1,2] used the moving chemical reaction boundary method (MCRBM) for the displacement separation of metal ions. Pospichol et al. [3] used the stationary neutralization reaction boundary method (SNRBM) for the investigation of mechanism of isoelectric focusing (IEF) [8–11] in CE. The authors [12–14] utilized the concept of MCRB for the development of the dynamic theory of classic IEF [8–11], the study on the instability of pH gradient occurring in the IEF [12,15–20] and the exploration of Hjerten's pH gradient mobilization in capillary isoelectric focusing (cIEF) [21–23]. The MCRBM has been used in the preparation of colloids and nano-particle materials [24]. Further, the instant MCRBM has been designed for the on-line improvement of resolution of separation in capillary zone electrophoresis as performed by Schwer (see Fig. 1C in ref. [25]).

There are the following experiments that demonstrate the validity of the theory of MCRB. The experiment of "precipitate reactive front" by Deman-Rigole [1,2] proved the existence of MCRB concept qualitatively. The experiments of electrically controlled electro-focusing by Pospichol et al. [3] quantitatively proved the validity of stationary neutralization reaction boundary equation deduced from the MCRBE [6,12]. The experiments of MCRB formed with cobaltic and hydroxyl ions by the authors [26,27] confirmed the theory of MCRB exactly. The author's recent experimental results of moving neutralization reactive boundary (MNRB) formed by strong acid and alkali further manifested the validity of the theory quantitatively [28,29]. However, the authors [30] found the non-validity of MCRBE for such a MCRB formed with the weak electrolytic system joined with an excess of background electrolyte KCl, corrected the original MCRBE and tested the validity of the corrected MCRBE for the given experimental conditions. The finding of non-validity of MCRBE for the weak electrolyte system indicates the necessary of further investigation on the MCRB theory and its related concepts like "constituent mobility" (see Section 4).

The purpose of the report is to further explore the validity of MCRBE for the system formed with weak acid and strong alkali joined with 0.1 M KCl. Interestingly, the paper shows the coexistence of

both the validity and non-validity of MCRBE for the MCRB composed with the mentioned system. Here we report the findings, give the corrected MCRBE and prove the correction of the equation.

## 2. Experimental

The Reagents used here are NaOH, acetic acid (HAc), KCl, bromophenol blue and agarose, the former three are analytical grade (purchased from Shanghai Chemical Reagents, Shanghai, China), the bromophenol is a chemical grade (CG) (purchased from Shanghai Chemical Reagents) and agarose is biochemical reagent (purchased from Shanghai Huang-Hua Pharmaceutical Factory, Shanghai, China).

The laboratory-made apparatus was used here, which was described in Refs. [27–29]. The electrolyte continuous flow-moving chemical reaction boundary method (ECF-MCRBM) employed here is according to the procedure reported in Refs. [28–30]. In the runs of MNRB moving towards the cathode, the initial  $\alpha$  phase contains HAc and 0.1 M KCl, and the initial  $\beta$  phase holds NaOH, 0.1 M KCl, 0.1% (w/v) bromophenol blue (BPB, only in the tube) and 1% (w/v) agarose gel (only in the tube). Whereas, in the runs towards the anode, the initial  $\alpha$  phase has HAc, 0.1 M KCl, 0.1% BPB (only in the tube) and 1% agarose gel (only in the tube), and the  $\beta$  phase comprises NaOH and 0.1 M KCl. The neutralization reaction of electromigration occurs in the 1% agarose gel of the tube as shown in Figs. 1 and 2 in Ref. [28]. The experimental results of MNRB formed with HAc and NaOH are shown in Figs. 1–3 and in Tables 1–5.

Here, the BPB is used as an indicator for the acetic zone (yellow), NaOH zone (blue) and the boundary between the two colors. As an acid-alkali indicator, the pH interval of BPB color transition is pH 3.1–4.6. In this paper, the pH value of the solution containing HAc is about pH 3, and that of the solution containing NaOH is near pH 11. So the BPB can be used for distinguishing the acetic and NaOH zones, and the boundary between the two zones. Before runs or after runs (viz., without the electric field), it was observed by the authors that the boundaries were blur, the colors of the boundary

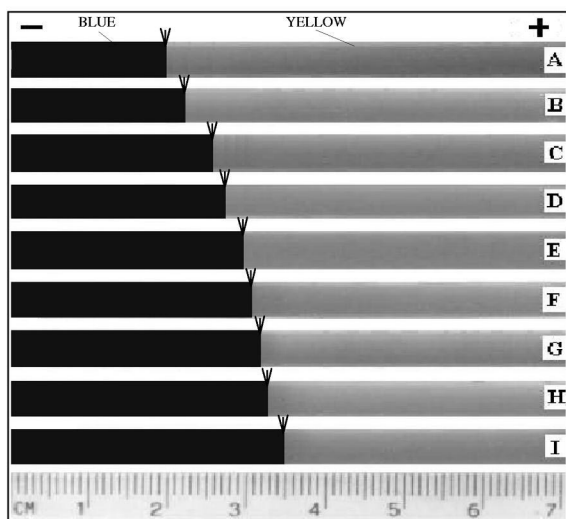


Fig. 1. The 10-min anodic movements of MCRB created with NaOH and HAc under the existence of 0.1 M KCl. Conditions: phase  $\alpha$  containing 0.1 M KCl+0.004 M HAc; phase  $\beta$  having 0.1 M KCl+A 0.0030 M, or B 0.0035 M, or C 0.0040 M, or D 0.0045 M, or E 0.0050 M, or F 0.0055 M, or G 0.0060 M, or H 0.0065 M, I 0.0070 M NaOH; 1% agarose gel; 0.1% bromophenol blue; current intensity=0.6 mA/mm<sup>2</sup>; run time=10 min; ID of tube=4.2–5.0 mm; length of tube=90 mm; flow-rate of anolyte and catholyte=0.6 ml/min. The anode is on the right and the cathode on the left.

range from yellow, to weak brown, to strong umber and to blue, the boundaries were wide (up to 1 mm, even to 3 mm after run about 5 min) due to the gradual ionic diffusive reaction existing in the

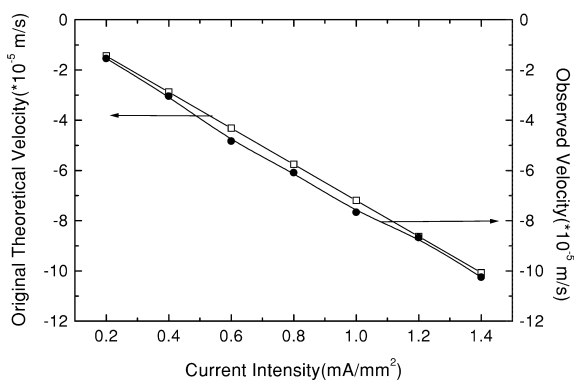


Fig. 2. The comparisons between the observed and original theoretical velocities of the anodic moving MNRB under different current intensity. Conditions: 0.004 M HAc, 0.005 M NaOH. The other conditions are all the same as those in Fig. 1.

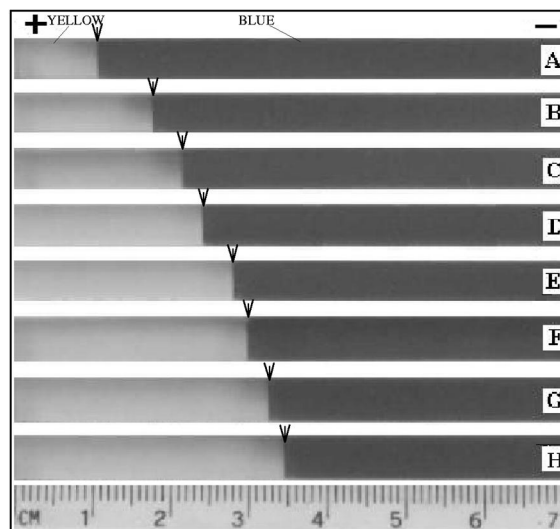


Fig. 3. The 10-min cathodic movements of MCRB created with NaOH and HAc under the existence of 0.1 M KCl. Conditions: phase  $\alpha$  containing 0.1 M KCl+A 0.03 M, or B 0.04 M, or C 0.05 M, or D 0.06 M, or E 0.07 M, or F 0.08 M, or G 0.09 M, or H 0.10 M HAc; phase  $\beta$  having 0.1 M KCl+0.001 M NaOH; 1% agarose gel; 0.1% bromophenol blue; current intensity=0.6 mA/mm<sup>2</sup>; run time=10 min; I.D. of tube=4.6–5.2 mm; length of tube=90 mm; flow-rate of anolyte and catholyte=0.6 ml/min. The anode is on the left and the cathode on the right.

boundaries. However, after the restore of electric field, the blur boundaries become sharp and clear rapidly (within about 30 s), those can be directly observed, in Figs. 1 and 3 here, Fig. 2 in Ref. [28], and Figs. 2 and 3 in Ref. [30]. Those results directly show that the ionic diffusion in the boundary possesses very weak influence on the boundary and its movement as compared with ionic electromigration. The further experimental investigations on MNRB [25] show that the strongest influence factors are the temperature, current intensity (CI) and the product between CI and  $t$  (time), which can cause great differences between the theoretical and experimental boundary velocities. The weak influence of ionic diffusion on boundary movement had been directly observed in moving boundary system (MBS) by MacInnes and Longworth (see Tables 2 and 3 in Ref. [31]). This was further proved by the authors with the comparisons between the ionic diffusive and electro-migrating fluxes in MBS or isotachopheresis [32,33].

Table 1

The comparisons between the observed and original theoretical velocities of the anodic moving MCRB created with 0.003–0.007 M NaOH and 0.4 M HAc under the existence of 0.1 M KCl<sup>a</sup>

Alphabets <sup>b</sup>	A	B	C	D	E	F	G	H	I
Phase $\alpha=0.1$ M KCl									
+ [HAc] (M)	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
[H <sup>+</sup> ] (M) <sup>c</sup>	0.000265	0.000265	0.000265	0.000265	0.000265	0.000265	0.000265	0.000265	0.000265
Phase $\beta=0.1$ M KCl									
+ [NaOH] (M)	0.003	0.0035	0.004	0.0045	0.005	0.0055	0.006	0.0065	0.007
$\mu_{\text{obs}}$ ( $\times 10^{-5}$ m/s)	<b>-3.46</b>	<b>-3.83</b>	<b>-4.08</b>	<b>-4.50</b>	<b>-4.83</b>	<b>-5.04</b>	<b>-5.17</b>	<b>-5.38</b>	<b>-5.67</b>
$\mu_{\text{ori}}$ (Eq. (13)) ( $\times 10^{-5}$ m/s)	<b>-3.10</b>	<b>-3.47</b>	<b>-3.79</b>	<b>-4.07</b>	<b>-4.31</b>	<b>-4.54</b>	<b>-4.74</b>	<b>-4.92</b>	<b>-5.08</b>
$\mu_{\text{obs}}/\mu_{\text{ori}}$	<b>1.11</b>	<b>1.11</b>	<b>1.08</b>	<b>1.11</b>	<b>1.12</b>	<b>1.11</b>	<b>1.09</b>	<b>1.09</b>	<b>1.12</b>

<sup>a</sup> The experiments are the same as those in Fig. 1.

<sup>b</sup> The alphabets in row 1 are correspondent to those in Fig. 1.

<sup>c</sup> The equilibrium constant of dissociation of HAc solution is  $1.76 \cdot 10^{-5}$  at 25°C [34].

Table 2

The comparisons between the observed and original theoretical velocities of the anodic moving MCRB created with 0.003 M NaOH and 0.001–0.007 M HAc under the existence of 0.1 M KCl<sup>a</sup>

Run	1	2	3	4	5	6	7
Phase $\alpha=0.1$ M KCl							
+ [HAc] (M)	0.001	0.002	0.003	0.004	0.005	0.006	0.007
[H <sup>+</sup> ] (M) <sup>b</sup>	0.000132	0.000187	0.000229	0.000265	0.000296	0.000324	0.000350
Phase $\beta=0.1$ M KCl							
+ [NaOH] (M)	0.003	0.003	0.003	0.003	0.003	0.003	0.003
$\mu_{\text{obs}}$ ( $\times 10^{-5}$ m/s)	<b>-6.54</b>	<b>-5.13</b>	<b>-4.04</b>	<b>-3.42</b>	<b>-2.83</b>	<b>-2.50</b>	<b>-2.04</b>
$\mu_{\text{ori}}$ (Eq. (13)) ( $\times 10^{-5}$ m/s)	<b>-5.94</b>	<b>-4.58</b>	<b>-3.71</b>	<b>-3.10</b>	<b>-2.66</b>	<b>-2.31</b>	<b>-2.04</b>
$\mu_{\text{obs}}/\mu_{\text{ori}}$	<b>1.10</b>	<b>1.11</b>	<b>1.08</b>	<b>1.10</b>	<b>1.07</b>	<b>1.08</b>	<b>1.00</b>

<sup>a</sup> Conditions: 0.003 M NaOH, 0.001–0.007 M HAc for the run from 1 to 7 respectively. The other conditions are the same as those in Fig.

1.

<sup>b</sup> The equilibrium constant of dissociation of HAc solution is  $1.76 \cdot 10^{-5}$  at 25°C [34].

Table 3

The comparisons between the observed, original theoretical and corrected theoretical velocities of the cathodic moving MCRB created with 0.03–0.10 M HAc and 0.001 NaOH under the existence of 0.1 M KCl in 1% agarose gel<sup>a</sup>

Alphabet <sup>b</sup>	A	B	C	D	E	F	G	H
Phase $\alpha=0.1$ M KCl								
+ [HAc] (M)	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
[H <sup>+</sup> ] (M) <sup>c</sup>	0.000725	0.000868	0.000936	0.00103	0.00111	0.00119	0.00126	0.00132
Phase $\beta=0.1$ M KCl								
+ [NaOH] (M)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$\mu_{\text{obs}}$ ( $\times 10^{-5}$ m/s)	<b>1.83</b>	<b>2.88</b>	<b>3.54</b>	<b>4.13</b>	<b>4.71</b>	<b>5.08</b>	<b>5.38</b>	<b>5.75</b>
$\mu_{\text{ori}}$ ( $\times 10^{-5}$ m/s) (Eq. (13))	<b>0.08</b>	<b>0.10</b>	<b>0.11</b>	<b>0.12</b>	<b>0.12</b>	<b>0.12</b>	<b>0.12</b>	<b>0.11</b>
$\mu_{\text{obs}}/\mu_{\text{ori}}$	<b>23</b>	<b>28</b>	<b>32</b>	<b>36</b>	<b>40</b>	<b>43</b>	<b>46</b>	<b>50</b>
$\mu_{\text{cor}}$ ( $\times 10^{-5}$ m/s) (Eq. (18))	<b>1.42</b>	<b>2.26</b>	<b>2.92</b>	<b>3.47</b>	<b>3.92</b>	<b>4.32</b>	<b>4.67</b>	<b>4.98</b>
$\mu_{\text{obs}}/\mu_{\text{cor}}$	<b>1.29</b>	<b>1.27</b>	<b>1.21</b>	<b>1.19</b>	<b>1.20</b>	<b>1.18</b>	<b>1.15</b>	<b>1.16</b>

<sup>a</sup> The experiments are the same as those in Fig. 3.

<sup>b</sup> The alphabets in row 1 are correspondent to those in Fig. 3.

<sup>c</sup> The equilibrium constant of dissociation of HAc solution is  $1.76 \cdot 10^{-5}$  at 25°C [34].

Table 4

The comparisons between the observed, original theoretical and corrected theoretical velocities of the cathodic moving MCRB created with 0.03–0.10 M HAc and 0.001 NaOH under the existence of 0.1 M KCl in 1% agarose gel<sup>a</sup>

Run	1	2	3	4	5	6	7	8	9
Phase $\alpha=0.1$ M KCl									
+ [HAc] (M)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
[H <sup>+</sup> ] (M) <sup>b</sup>	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375
Phase $\beta=0.1$ M KCl									
+ [NaOH](M)	0.001	0.0015	0.002	0.0025	0.003	0.0035	0.004	0.0045	0.005
$\mu_{\text{obs}}$ ( $\times 10^{-5}$ m/s)	<b>10.83</b>	<b>9.67</b>	<b>7.92</b>	<b>6.50</b>	<b>5.41</b>	<b>4.29</b>	<b>3.50</b>	<b>2.63</b>	<b>1.96</b>
$\mu_{\text{ori}}$ ( $\times 10^{-5}$ m/s)(Eq. (13))	<b>0.06</b>	<b>0.05</b>	<b>0.05</b>	<b>0.04</b>	<b>0.04</b>	<b>0.03</b>	<b>0.03</b>	<b>0.02</b>	<b>0.02</b>
$\mu_{\text{obs}}/\mu_{\text{ori}}$	<b>180</b>	<b>176</b>	<b>160</b>	<b>147</b>	<b>140</b>	<b>128</b>	<b>124</b>	<b>115</b>	<b>112</b>
$\mu_{\text{cor}}$ ( $\times 10^{-5}$ m/s)(Eq. (18))	<b>10.18</b>	<b>8.39</b>	<b>6.92</b>	<b>5.68</b>	<b>4.62</b>	<b>3.71</b>	<b>2.92</b>	<b>2.22</b>	<b>1.61</b>
$\mu_{\text{obs}}/\mu_{\text{cor}}$	<b>1.06</b>	<b>1.15</b>	<b>1.14</b>	<b>1.15</b>	<b>1.17</b>	<b>1.16</b>	<b>1.20</b>	<b>1.18</b>	<b>1.22</b>

<sup>a</sup> Conditions: 0.001–0.005 M NaOH for the run from 1 to 9 respectively, 0.8 M HAc. The other conditions are the same as those in Fig. 3.

<sup>b</sup> The equilibrium constant of dissociation of HAc solution is  $1.76 \cdot 10^{-5}$  at 25°C [34].

The MCRBE for the system of weak reactive electrolytes, such as  $\text{NH}_3\text{H}_2\text{O}$  and HAc, as originally formulated by the authors [4–7], is:

$$\frac{\bar{m}_{\text{H}^+}^{\alpha} \bar{c}_{\text{H}^+}^{\alpha}}{\kappa^{\alpha}} - \frac{\bar{m}_{\text{OH}^-}^{\beta} \bar{c}_{\text{OH}^-}^{\beta}}{\kappa^{\beta}} = \nu^{\alpha\beta} (\bar{c}_{\text{H}^+}^{\alpha} - \bar{c}_{\text{OH}^-}^{\beta}) \quad (1)$$

where,  $\kappa$  is the specific conductivity of a phase (in:  $\text{S} \cdot \text{m}^{-1}$ ), and  $\nu^{\alpha\beta}$  is the boundary displacement per-Coulomb of electric charge (in:  $\text{m}^3 \cdot \text{C}^{-1}$ ), the superscripts  $\alpha$  and  $\beta$  indicate phase  $\alpha$  and  $\beta$  respectively,  $\bar{m}_{\text{H}^+}$  and  $\bar{c}_{\text{H}^+}$  are respectively hydrogen “constituent mobility” (in:  $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ ) and “constituent concentration” (in: equiv.  $\text{m}^{-3}$ ),  $\bar{m}_{\text{OH}^-}$  and  $\bar{c}_{\text{OH}^-}$  are respectively hydroxyl “constituent mobility” and “constituent concentration”. As defined by Tiselius and Alberty [9], for a weak electrolyte the “constituent mobility” is written as:

$$\bar{m} = \sum a_i m_i \quad (2)$$

and “constituent concentration” is given as:

$$\bar{c} = \sum c_i \quad (3)$$

$$a_i = \frac{c_i}{\bar{c}} = \frac{c_i}{\sum c_i} \quad (4)$$

where,  $m_i$  and  $c_i$  are, respectively, the mobility and concentration of sub-species  $i$ ,  $a$  is the fraction of sub-species  $i$  with mobility  $m_i$ .

With the aid of the example of HAc solution, it will be shown the applications of Eqs. (2) and (3) to the HAc solution. For the HAc solution, there is the following chemical equilibrium:

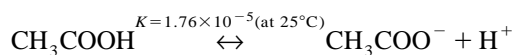


Table 5

The comparisons between the observed, original theoretical and corrected theoretical velocities of the cathodic moving MCRB created with 0.8 M HAc and 0.001 NaOH under the existence of 0.1 M KCl under different current intensity<sup>a</sup>

Current intensity ( $i$ , mA/mm <sup>2</sup> ) <sup>b</sup>	0.1	0.2	0.3	0.4	0.5	0.6
$\mu_{\text{obs}}$ ( $\times 10^{-5}$ m/s) <sup>b,c</sup>	<b>1.83</b>	<b>3.67</b>	<b>5.79</b>	<b>7.73</b>	<b>9.08</b>	<b>10.83</b>
$\mu_{\text{ori}}$ ( $\times 10^{-5}$ m/s) (Eq. (13))	<b>0.01</b>	<b>0.02</b>	<b>0.03</b>	<b>0.04</b>	<b>0.05</b>	<b>0.06</b>
$\mu_{\text{obs}}/\mu_{\text{ori}}$	<b>182.00</b>	<b>182.00</b>	<b>188.00</b>	<b>182.00</b>	<b>181.00</b>	<b>180.00</b>
$\mu_{\text{cor}}$ ( $\times 10^{-5}$ m/s) (Eq. (18)) <sup>c</sup>	<b>1.70</b>	<b>3.39</b>	<b>5.09</b>	<b>6.79</b>	<b>8.49</b>	<b>10.18</b>
$\mu_{\text{obs}}/\mu_{\text{cor}}$	<b>1.08</b>	<b>1.08</b>	<b>1.11</b>	<b>1.08</b>	<b>1.07</b>	<b>1.06</b>

<sup>a</sup> Conditions: 0.001 M NaOH, 0.8 M HAc and 0.1–0.6 mA/mm<sup>2</sup>. The other conditions are the same as those in Fig. 3.

<sup>b</sup> The linear regression between  $i$  and  $\mu_{\text{obs}}$  is:  $\mu_{\text{obs}} = 17.98i + 0.11$  ( $R=0.99966$ ,  $\text{SD}=0.09877$ ,  $N=6$ ).

<sup>c</sup> The linear regression between  $\mu_{\text{obs}}$  and  $\mu_{\text{cor}}$  is:  $\mu_{\text{cor}} = 0.94\mu_{\text{obs}} - 0.10$  ( $R=0.99966$ ,  $\text{SD}=0.09322$ ,  $N=6$ ).

where, the  $K$  is the equilibrium constant of dissociation of HAC solution ( $=1.76 \cdot 10^{-5}$  at  $25^\circ\text{C}$ ) [34]. According to Eq. (3), the “hydrogen constituent concentration” for HAC solution is:

$$\bar{c}_{\text{H}^+} = \sum c_i = c_{\text{H}^+} + c_{\text{CH}_3\text{COOH}} \quad (5)$$

and according to Eq. (2) the “hydrogen constituent mobility” of HAC solution is:

$$\begin{aligned} \bar{m}_{\text{H}^+} &= \sum a_i m_i = \frac{c_{\text{H}^+}}{c_{\text{H}^+}} m_{\text{H}^+} + \frac{c_{\text{CH}_3\text{COOH}}}{c_{\text{H}^+}} m_{\text{CH}_3\text{COOH}} \\ &= \frac{(c_{\text{H}^+} m_{\text{H}^+} + c_{\text{CH}_3\text{COOH}} m_{\text{CH}_3\text{COOH}})}{\bar{c}_{\text{H}^+}} \end{aligned} \quad (6)$$

The combination of Eqs. (5) and (6) yields:

$$\bar{m}_{\text{H}^+} \bar{c}_{\text{H}^+} = m_{\text{H}^+} c_{\text{H}^+} + m_{\text{CH}_3\text{COOH}} c_{\text{CH}_3\text{COOH}} \quad (7)$$

In Eq. (7) there exist  $m_{\text{CH}_3\text{COOH}} = 0$  due to zero-charge of HAC [9], so one obtain:

$$m_{\text{CH}_3\text{COOH}} c_{\text{CH}_3\text{COOH}} = 0 \quad (8)$$

Therefore, the joining between Eqs. (7) and (8) produces:

$$\bar{m}_{\text{H}^+} \bar{c}_{\text{H}^+} = m_{\text{H}^+} c_{\text{H}^+} \quad (9)$$

For the strong alkali of NaOH, the “hydroxyl constituent mobility” equals the actual mobility of hydroxyl ion and the “hydroxyl constituent concentration” is just the concentration of hydroxyl ion due to almost complete dissociation of diluted strong electrolyte. So as treated by Alberty [9], one obviously has:

$$\bar{m}_{\text{OH}^-} \bar{c}_{\text{OH}^-} = m_{\text{OH}^-} c_{\text{OH}^-} \quad (10)$$

$$\bar{c}_{\text{OH}^-} = c_{\text{OH}^-} \quad (11)$$

For the investigated electrolytic system composed with HAC and NaOH, because the weak alkali is displaced by the strong alkali NaOH. Hence inserting Eqs. (9)–(11) into Eq. (1), one obtains:

$$\frac{m_{\text{H}^+} c_{\text{H}^+}^\alpha}{\kappa^\alpha} - \frac{m_{\text{OH}^-} c_{\text{OH}^-}^\beta}{\kappa^\beta} = \nu^{\alpha\beta} (\bar{c}_{\text{H}^+}^\alpha - c_{\text{OH}^-}^\beta) \quad (12)$$

Therefore, the original theoretical velocity of boundary, which is transformed from Eq. (12) as has

been similarly shown in Ref. [6], for the MCRB formed with  $\text{CH}_3\text{COOH}$  and NaOH, is given as:

$$\mu_{\text{ori}}^{\alpha\beta} = i \left( \frac{m_{\text{H}^+} c_{\text{H}^+}^\alpha}{\kappa^\alpha} - \frac{m_{\text{OH}^-} c_{\text{OH}^-}^\beta}{\kappa^\beta} \right) / (c_{\text{H}^+}^\alpha - \bar{c}_{\text{OH}^-}^\beta) \quad (13)$$

In Eq. (13),  $\mu_{\text{ori}}^{\alpha\beta}$  is the original velocity of boundary  $\alpha\beta$  (in: m/s),  $i$  the current intensity (in: mA/mm<sup>2</sup>).

The ionic mobilities in Eqs. (12)–(13) should be corrected with the empirical equation:

$$\begin{aligned} m_{\text{act}} &= m_0 \exp\left( -\eta \sqrt{zI} \right) \quad (z = 1, \eta = 0.5; z \geq 2, \eta = 0.77) \\ & \quad (14) \end{aligned}$$

$$I = 0.5 \sum_i c_i z_i^2 \quad (15)$$

which is of validity for large organic ion with low electric charge intensity [35–37] and small inorganic ion with high electric charge intensity [38,39], if ionic strength is not over 0.1  $M$  obviously. In Eq. (14),  $m_{\text{act}}$  is the actual ionic mobility,  $m_0$  the absolute ionic mobility,  $z$  the ionic charge(s) and  $I$  the ionic strength. The absolute mobilities of hydrogen and hydroxyl ions at  $25^\circ\text{C}$ , cited from Ref. [40], are respectively 36.3 and  $20.5 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

Owing to very high concentration of KCl, here exists  $\kappa^\alpha = \kappa^\beta = 1.22 \text{ S/m}$  (the runs were performed at about  $18\text{--}20^\circ\text{C}$ ), as have been treated earlier [1–3,25–29].

The experimental data are all treated with the two softwares Original (ver. 5.0, Microcal Co.) and Excel (ver. 97, Microsoft, USA).

### 3. Results

#### 3.1. Results for anodic moving MNRB

According to the ECF-MCRBM described in Refs. [27–29], we performed the experiments of anodic movement of MCRB created by NaOH and HAC under the existence of KCl in large concentration. The movement of each MNRB was shown in Fig. 1. The length ( $l_{\text{obs}}$ ) of anodic movement of MCRB, which is the length of the blue zone from the cathode

end to the mark arrows, can be directly monitored. The observed velocity ( $\mu_{\text{obs}}$ ) was calculated with:

$$\mu_{\text{obs}} = l_{\text{obs}}/t \quad (16)$$

where,  $t$  is the time consumed (=600 s here). The observed velocities of boundary in Fig. 1 are given in Table 1. The alphabets of Table 1 correspond to those in Fig. 1.

The original theoretical values of the anodic moving MNRB computed by Eq. (13) for the experiments of Fig. 1 are also displayed in Table 1.

Table 1 shows the comparisons between the experimental and theoretical velocities of anodic movement of MNRB formed with 0.003–0.007  $M$  NaOH and 0.4  $M$   $\text{CH}_3\text{COOH}$ , together with an excess of KCl. Comparing the original theoretic velocities computed by Eq. (13) with the observed velocities by Eq. (16), one can obviously find the ratios between the observed and original theoretic velocities range from 1.08 to 1.12, being very near to one. The results imply good agreement existing between the observed and original theoretic velocities computed by Eq. (13). Therefore, Eqs. (12) and (13) possess the validity for the anodic moving MNRB under the given experimental conditions. The conclusion is further demonstrated by the following comparisons in Table 2.

As given in Table 2, the anodic moving MNRB was formed with the alkali of 0.003  $M$  NaOH and the acid of HAc ranging from 0.001 to 0.007  $M$ , coupled with 0.1  $M$  KCl. The other experimental conditions are the same as those in Fig. 1. The ratio between the observed and predicted velocities are over one very slightly. This also indicates the excellent agreement between the experimental results and the original theoretical computation with Eq. (13).

If changing the current intensity, one can also obtain the exactly quantitative coincidence between the observed and original theoretical velocities existing in the anodic moving MNRB in Fig. 2. Eq. (13) shows that the increase of current intensity leads to the linear augmentation of boundary velocity ( $\square$ - -  $\square$ ). As verified in Fig. 2, when the current intensity rises, both the observed and original theoretical velocities raise linearly and there is present high quantitative agreement between the observed ( $\bullet$ - -  $\bullet$ ) and theoretical ( $\square$ - -  $\square$ ) boundary velocities.

### 3.2. Results for cathodic moving MNRB

The authors also carried out the experiments of cathodic movement of MCRB created with the same electrolytic system but with different concentration. The boundary movements of our first group run are displayed in Fig. 3. According to the boundary movement in Fig. 3, we calculated the observed velocity of boundary, the results are shown in Table 3. It is obvious in Table 3 that the ratios of the observed and original theoretic values computed with Eq. (13) change from 23 to 50, much high values of the ratio. The ratios demonstrate that the observed velocities of MNRB are completely in disagreement with the original theoretic values computed by Eq. (13). Hence, Eq. (13) also holds no validity for the cathodic movement of MNRB formed by the weak acid HAc and the strong base NaOH under the existence of 0.1  $M$  KCl. Under the given experimental conditions of Fig. 3, the experimental results demonstrate that Eqs. (12) and (13) should be corrected as, respectively:

$$\frac{m_{\text{H}^+}^{\alpha} c_{\text{H}^+}^{\alpha}}{\kappa^{\alpha}} - \frac{m_{\text{OH}^-}^{\beta} c_{\text{OH}^-}^{\beta}}{\kappa^{\beta}} = \nu_{\text{cor}}^{\alpha\beta} (c_{\text{H}^+}^{\alpha} - c_{\text{OH}^-}^{\beta}) \quad (17)$$

$$\mu_{\text{cor}}^{\alpha\beta} = i \left( \frac{m_{\text{H}^+}^{\alpha} c_{\text{H}^+}^{\alpha}}{\kappa^{\alpha}} - \frac{m_{\text{OH}^-}^{\beta} c_{\text{OH}^-}^{\beta}}{\kappa^{\beta}} \right) / (c_{\text{H}^+}^{\alpha} - c_{\text{OH}^-}^{\beta}) \quad (18)$$

Eqs. (17) and (18) are just the MCRBE originally used to a strong electrolytic system, such as  $\text{CoCl}_2$ –NaOH [24,26,27] and HCl–NaOH [28,29], but now used to the system of NaOH–HAc in excess of KCl. Comparing Eq. (13) with Eq. (18), the only difference is: there is a bar over  $c_{\text{H}^+}$  in the denominator of Eq. (13), but no the bar in Eq. (18). Those are also shown in Eqs. (12) and (17).

The corrected theoretic velocities by Eq. (18) for the experiments in Fig. 3 are also given in Table 3. It is shown in Table 3, the good coincidence exists between the observed results of Fig. 3 and the corrected theoretic velocities by Eq. (18): the ratio change only from 1.15 to 1.29 closing to one. Those results directly show the validity of the corrected equation, viz., Eq. (18), for the cathodic experiments of MNRB in Fig. 3.

Evidently, from the above comparisons in Table 3, one can achieve two interesting findings, one is the non-validity of the original MNRBE (viz., Eqs. (12) and (13)) for the cathodic migrating MNRB created with NaOH and HAc coupled with 0.1 M KCl and the another is the validity of the corrected MCRBE (viz., Eqs. (17) and (18)) for the given conditions in Fig. 3. The following results in Tables 4 and 5 will further confirm the two findings for the cathodic migrating MNRB.

Table 4 also exhibits the comparisons between the observed, original and corrected theoretical velocities of the cathodic moving MNRB being similar to that of Table 3. It is clear there are present extremely high ratio between the observed and original velocities (from near 112 to about 180), but good ratio between the observed and corrected velocities (from 1.06 to 1.22, near to one). Those results evidently proved the two achieved findings above — the non-validity of the original MCRBE (viz., Eqs. (12) and (13)) and the validity of the corrected MCRBE (viz., Eqs. (17) and (18)) for the cathodic moving MNRB under the given conditions. Those are further confirmed by the results of comparisons between the observed, original and corrected theoretical velocities in Table 5 in which the runs were performed under different current intensity from 0.1 to 0.6 mA/mm<sup>2</sup>.

As shown in Table 5, in the cathodic moving MNRB created under the given conditions: (1) there are very poor coincidences between the observed and original theoretical velocities: the ratio between them changing from 180 to 188, extremely high values; (2) but there are present excellent agreements between the observed and corrected theoretical velocities: the ratio being 1.06–1.11 and the linear regression equation being  $\mu_{\text{cor}} = 0.94\mu_{\text{obs}} - 0.10$  ( $R = 0.99966$ ,  $SD = 0.09322$ ,  $N = 6$ ); (3) there exist a high linear regression between current intensity ( $i$ ) and the observed velocity:  $\mu_{\text{obs}} = 17.98i + 0.11$  ( $R = 0.99966$ ,  $SD = 0.09877$ ,  $N = 6$ ), this directly proved the correct prediction of Eq. (18) — the increase of current intensity leads to the linear increment of boundary velocity.

#### 4. Discussions and Conclusions

From the results in Section 3.1, it is evident that,

the original MCRBE, viz., Eqs. (12) and (13), hold validity for the anodic movement of MNRB formed with HAc and NaOH coupled with 0.1 M KCl, if the MNRB is an anodic moving boundary (see Tables 1 and 2 and Figs. 1 and 2). However, if the MNRB is a cathodic moving boundary, the original MCRBE, viz., Eqs. (12) and (13), are not valid for the MNRB under the given conditions (see Tables 3–5 and Fig. 3). Evidently, both the validity and non-validity of the original MCRBE are respectively present for the anodic and cathodic moving MNRB formed with HAc and NaOH together with an excess of KCl. In other words, the validity and non-validity of the MCRBE co-exist respectively for the anodic and cathodic moving MNRBs formed under given conditions. The found fact is clearly different from the previous one — the complete non-validity of the original MCRBE for the MNRB created with weak acid–weak base in the excess existence of KCl [30].

For the cathodic moving boundary, the original MCRBE (Eqs. (12) and (13)) should respectively be corrected as Eqs. (17) and (18), which hold clear validity for the cathodic moving MNRB composed with HAc and NaOH under an excess of KCl. The comparisons in Tables 3–5 directly manifest the correction of the corrected MCRBE (viz., Eqs. (17) and (18)).

The facts — the original MCRBE of Eqs. (12) and (13) possess the validity for the anodic moving MNRB in Tables 1 and 2 and Figs. 1 and 2, but non-validity for the cathodic moving MNRB in Tables 3–5 and Fig. 3, and Eqs. (12) and (13) ought to be respectively corrected as Eqs. (17) and (18) for the cathodic moving MNRB in Tables 3–5 and Fig. 3 — indirectly imply the non-validity of the very old concepts of “constituent mobility” (see Eq. (2)) and “constituent concentration” (see Eq. (3)) under the existence of KCl in large concentration. The two old concepts, firstly advocated by Tiselius and Alberty [9], were used for the electromigration study of weak electrolyte like the HAc studied here. According to the two concepts, a weak electrolyte electro-migrates as “a whole group”. However, the facts in this paper indirectly imply that under large concentration KCl the weak electrolyte does not electro-migrates as “a whole group”, but moves with “sub-species” as a group. Whereas, the facts can not directly prove the non-validity of Eqs. (2) and (3) (viz., the two old



concepts). To do so, one must precisely measure all components of two phases in a MNRB created with at least one weak electrolyte. The present MNRBM can not be used for the determination of all components of two phases, since when one remove the gel from the tube, one of the two phases in the gel is seriously contaminated by the another phase. Therefore, in order to explore the validity of two concepts of Eqs. (2) and (3) under the given conditions, new

MNRBM must be developed to overcome the serious contamination.

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### Appendix A. Theoretical computing procedures of boundary velocity

A [ Calculation of  $I$  with Eq. (15) ]  
[\*Note: the existence of KCl ]

↓

$$\left[ \begin{array}{l} \text{Calculation of } m_{\text{act}} \text{ with Eq. (14) from} \\ m_{0,\text{H}^+} = 36.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \\ m_{0,\text{OH}^-} = 20.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \\ \text{plus } i = 600 \text{ A m}^{-2} \\ \kappa^\alpha = \kappa^\beta = 1.22 \text{ S m}^{-1} \\ c_{\text{OH}^-} = [\text{NaOH}] = 0.003\text{--}0.007 \text{ M} \\ \bar{c}_{\text{H}^+} = [\text{CH}_3\text{COOH}] = 0.004 \text{ M} \end{array} \right]$$

↓ Insert data in Eq. (13)

[Calculation of MCRB with Eq. (13)]

B [ Calculation of  $I$  with Eq. (15) ]  
[\*Note: the existence of KCl ]

↓

$$\left[ \begin{array}{l} \text{Calculation of } m_{\text{act}} \text{ with Eq. (14) from} \\ m_{0,\text{H}^+} = 36.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \\ m_{0,\text{OH}^-} = 20.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \\ \text{plus } i = 600 \text{ A m}^{-2} \\ \kappa^\alpha = \kappa^\beta = 1.22 \text{ S m}^{-1} \\ c_{\text{OH}^-} = [\text{NaOH}] = 0.001 \text{ M} \\ \bar{c}_{\text{H}^+} = [\text{H}^+] = 0.000725\text{--}0.00132 \text{ M} \end{array} \right]$$

↓ Inset data into Eq. (18)

[Calculation of MCRB with Eq. (18)]

**A:** The original theoretical calculation of anodic moving boundary velocity (using the data in Table 1 as an example). **B:** the corrected theoretical computation of cathodic moving boundary velocity (using the data in Table 3 as example).

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