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Moving chemical reaction boundary and isoelectric focusing II. Existence of quasi/equal fluxes (or transference numbers) of hydrogen and hydroxyl ions in stationary electrolysis and Svensson's isoelectric focusing

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Abstract

By using some basic physico-chemical data, the fluxes (or transference numbers) of proton and hydroxyl ion in the stationary electrolysis are compared with the relative judgment expressions which were defined from moving chemical reaction boundary equations. The results reveal that the quasi/equal fluxes of hydrogen and hydroxyl ions are present in the neutralization reaction boundary formed with pure acid and base, in stationary electrolysis and in Svensson's isoelectric focusing (IEF). Thus, the findings are completely in agreement with the inference – the existence of quasi/equal fluxes of proton and hydroxyl ion in stationary electrolysis and Svensson's IEF – which is based upon the conditional equations for the anolyte and catholyte (equivalently, stationary neutralization reaction boundary equations) and upon the facts that the pH gradients in Svensson's IEF are quasi-stable, but not complete stable. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Based upon the ideas of 'precipitate reaction front' advanced by Deman and Rigole [1,2], and that of stationary neutralization reaction boundary (SNRB) developed by Pospichal and co-workers [3,4], the concepts of moving and stationary chemical reaction boundary (MCRB, SCRIB) were developed, and some moving chemical reaction boundary equations (MCRBEs), together with the stationary chemical reaction boundary equations (SCRBEs), were derived [5–7].

The theory of MCRB has been proved by some facts and experiments: (1) the analyses with station-

ary chemical reaction boundary equations are in agreement with the computer simulations based on Kohlrausch's *beharrliche* function and with the experiments of electrically controlled focusing in capillary electrophoresis by Pospichal et al. [3] quantitatively [6]; (2) the movements of precipitate reaction boundary, viz., the 'precipitate reaction front' as it has been called by Deman and Rigole [1,2], are in coincidence with the analyses with the MCRB theory qualitatively [8]; (3) the experimental velocities of MCRBs formed by CoCl_2 and NaOH , together with 0.01 M background electrolyte KCl , are compared with the theoretical velocities of MCRBs, the results show that there exist quantitative

agreement between the experimental and theoretical velocities of MCRBs formed by CoCl_2 and NaOH [9].

In the accompanying report [10], it was, theoretically and experimentally, shown that Svensson's isoelectric focusing (IEF) [11,12] is based on the stationary electrolysis, in which the electromigration reaction occurs between the hydrogen and hydroxyl ions migrating in opposite directions, and in which the neutralization reaction boundary is created by the hydrogen and hydroxyl ions; it was also inferred the quasi/equal fluxes (or transference numbers) of hydrogen and hydroxyl ions should be present in the stationary electrolysis and Svensson's IEF.

However, this inference has not been proved.

Therefore, the purpose of this report is to compare the fluxes of hydrogen and hydroxyl ions in stationary electrolysis, to reveal the existence of quasi/equal fluxes of hydrogen and hydroxyl ions in the stationary electrolysis upon which Svensson's IEF is based, and finally to show the validity of the inference given in the accompanying paper [10].

In order to compare the fluxes of proton in an acid and hydroxyl ion in a base, it is necessary to define the absolute expression

$$R_{\text{abs}} = m_+^{\alpha} c_+^{\alpha} \kappa^{\beta} - m_-^{\beta} c_-^{\beta} \kappa^{\alpha} \quad (1)$$

and the relative expressions from the MCRBEs [8,13]

$$R_r = \frac{m_+^{\alpha} c_+^{\alpha} \kappa^{\beta}}{m_-^{\beta} c_-^{\beta} \kappa^{\alpha}} - 1 = \frac{T_+^{\alpha}}{T_-^{\beta}} - 1 \quad (\text{for } R_{\text{abs}} \geq 0) \quad (2a)$$

$$R_r = 1 - \frac{m_-^{\beta} c_-^{\beta} \kappa^{\alpha}}{m_+^{\alpha} c_+^{\alpha} \kappa^{\beta}} = 1 - \frac{T_-^{\beta}}{T_+^{\alpha}} \quad (\text{for } R_{\text{abs}} < 0) \quad (2b)$$

where R = symbol of judgment expression, the subscripts, 'abs' and 'r', mean the absolute and relative values, respectively; κ = conductivity of a

solution or phase (S/m); m = mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$); T = transference number; c = concentration (equiv./l), the subscripts, '+' and '-', imply the positive and negative reacting ions, such as hydrogen and hydroxyl ions, respectively, and the superscripts, ' α ' and ' β ', mean phase α and β , respectively.

Clearly, if $R_r = 0$, one can get the stationary chemical reaction boundary equations (SCRBEs, see Eqs. (72)–(80) in Ref. [10]), including the conditional equations for the anolyte and catholyte (see Eqs. (65)–(68) in Ref. [10]), equivalently the stationary neutralization reaction boundary equations (SNRBEs, see Eqs. (77)–(80) in Ref. [10]). Thus, the significance of $R_r \cong 0$ is that the transference number (or flux) of the positive reacting ion, such as the hydrogen ion, is equal (or very near) to that of the negative reacting ion, for instance the hydroxyl ion.

2. Literature data and treatments (Table 1)

The molar conductivities of HCl and NaOH at 25°C originate from Ref. [14]. The absolute mobilities of hydrogen and hydroxyl ions in infinite diluted solutions at 25°C , which are 3.63 and $2.05 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, are quoted from Ref. [15].

Owing to the pure acid and base discussed here, the specific conductivity may be given as

$$\kappa = c\Lambda \quad (3)$$

where Λ is the molar conductivity of a pure solution ($\text{m}^2 \text{ S/mol}$).

Due to the existence of ionic strength I , the absolute mobilities of hydrogen and hydroxyl ions ought to be corrected with the following empirical equation, viz., Eq. (4), which is valid for both large ions with low electric charge intensity [16,17] and

Table 1

The molar conductivities ($10^{-2} \text{ S m}^2 \text{ mol}^{-1}$) of HCl and NaOH at different concentration at 25°C ^a

	Conc. (M)						
	Infinite	0.0001	0.0005	0.001	0.005	0.010	0.050
HCl	4.260	4.245	4.225	4.212	4.157	4.118	3.989
NaOH	2.477	—	2.455	2.446	2.407	2.379	—

^aThe molar conductivities of other acids, HBr , HI and H_2SO_4 , diluted infinitely also originate from Ref. [14] (but not shown here).

small ions, such as sodium ions and protons, with high electric charge intensity [18,19], if the ionic strength is not over 0.1 mol/l

$$m_{\text{act}} = m_0 \exp(-\eta\sqrt{zI}) \quad (\text{for } I \leq 0.1 \text{ mol/l},$$

and if $z = 1 \quad \eta = 0.5$, or if $z \geq 2 \quad \eta = 0.77$) (4)

where the subscripts, 'act' and '0', indicate the actual and absolute mobilities respectively, z the electric charge of ion, and I the ionic strength ($I = 0.5 \sum c_i z_i^2$, mol/l).

Thus, Eqs. (2a) and (2b), as will be used to compare the fluxes of hydrogen and hydroxyl ions, is changed as

$$R_r = \frac{m_{\text{act,H}^+} \Lambda_{\text{NaOH}}}{m_{\text{act,OH}^-} \Lambda_{\text{HCl}}} - 1 \quad (\text{for } R_{\text{abs}} \geq 0) \quad (5a)$$

$$R_r = 1 - \frac{m_{\text{act,OH}^-} \Lambda_{\text{HCl}}}{m_{\text{act,H}^+} \Lambda_{\text{NaOH}}} \quad (\text{for } R_{\text{abs}} < 0) \quad (5b)$$

In order to compute the ionic strength I , the actual mobilities of ions and the values of R_r , viz., Eqs. (5a) and (5b), a computer (486DX/80, 8 Mbyte RAM, 540 Mbyte hard disk, Copam Electronic Co., Taiwan, China) is used and a program is written in the QBASIC (Ver. 4.5, Microsoft, Redmond, WA, USA).

3. Results

3.1. Limited value of R_r for acids and bases diluted infinitely

Clearly, if HCl and NaOH are diluted infinitely, i.e., the concentrations of hydrogen and hydroxyl ions, together with the ionic strength I , are close to zero, one achieves a limited value of R_r

$$\lim_{\substack{C_{\text{H}^+} \rightarrow 0, \\ C_{\text{OH}^-} \rightarrow 0}} (R_r) = R_{r,0} = \frac{m_{0,\text{H}^+} \Lambda_{0,\text{NaOH}}}{m_{0,\text{OH}^-} \Lambda_{0,\text{HCl}}} - 1 = 0.030 \quad (6)$$

where the subscript, '0' means the limited values of R_r , ionic mobility and molar conductivity in infinite diluted solutions, viz., ionic strength near to zero.

Similarly, one also has the limited values of R_r for HBr and NaOH, HI and NaOH, and H_2SO_4 and

NaOH, diluted infinitely: $R_{r,0}$ (for HBr and NaOH) = 0.025; $R_{r,0}$ (for HI and NaOH) = 0.028; and $R_{r,0}$ (for H_2SO_4 and NaOH) = 0.020.

These data show that the values of R_r are very near to zero. Clearly, the results imply that the quasi/equal fluxes of hydrogen and hydroxyl ions exists in the neutralization reaction boundaries created by acid and base diluted infinitely.

3.2. Values of R_r for HCl and NaOH and for HBr and NaOH

The values of R_r for the equal-concentration HCl and NaOH are shown in Fig. 1. The results shows that the computed values of R_r for HCl and NaOH and for HBr and NaOH are less than 3%, a value very near to zero, and are quite constant with the synchronous enormous concentration increases from zero to 0.01 mol/l, as shown in Fig. 1.

The values of R_r for HCl and NaOH with different concentrations are shown in Fig. 2a and Fig. 2b. Fig. 2a shows the relation between the R_r and the concentration of HCl, and Fig. 2b displays the R_r as a function of the concentration of NaOH. Both Fig. 2a and Fig. 2b show that the values of R_r for HCl and NaOH are in general less than 5%, and in some cases equal to zero, regardless of whether the concentrations of HCl and NaOH are high or low.

It is clear from the data of R_r above that the transference number (or flux) of proton in an acid is almost equal to that of hydroxyl ion in a base, regardless of whether the concentrations of the acid and base are high or low, or are equal to each other. With the basic physico-chemical data in Tables 1 and

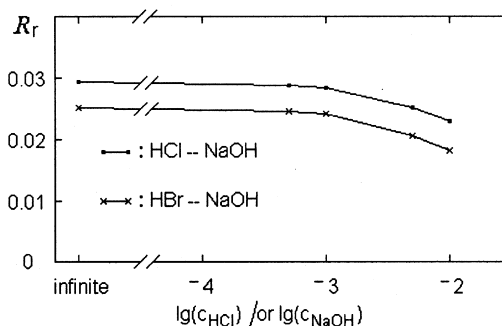


Fig. 1. The values of R_r for equal-concentration HCl and NaOH, and HBr and NaOH.

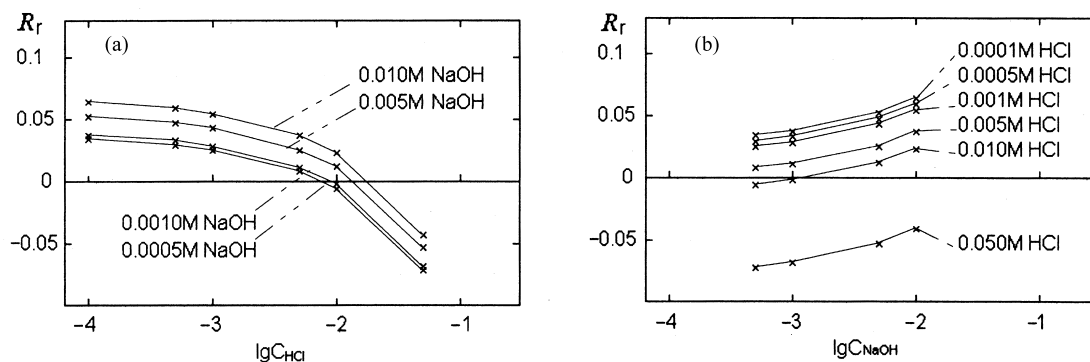


Fig. 2. The values of R_r for HCl and NaOH with different concentrations: (a) the dependence of the values on the concentration of HCl; (b) the dependence of the values on the concentration of NaOH.

2 in Ref. [20], we will show that the quasi-equal-fluxes of hydrogen and hydroxyl ions also exist in the system of weak acid and base [21].

4. Discussions and conclusions

Figs. 1 and 2 reveal that, if a boundary is formed with pure acid and base like HCl and NaOH, the fluxes of hydrogen and hydroxyl ions are almost equal to each other, regardless of whether their concentrations are high or low. The same results can also be obtained in other boundaries formed by acids and bases, such as HBr and NaOH, HI and NaOH, and H_2SO_4 and NaOH, if the ionic strength is less than 0.1 mol/l (not shown here).

As stated by Svensson [11] and Tiselius [12], during stationary electrolysis, the acid is accumulated in the anodic vessel, whereas the base is accumulated in the cathodic vessel. Obviously a neutralization reaction boundary is created in stationary electrolysis. Thus, the results in Figs. 1 and 2 also reveal the existence of quasi/equal transference numbers of hydrogen and hydroxyl ions in stationary electrolysis. With the basic physico-chemical data in Tables 1 and 2 in Ref. [20], it will be shown that the quasi/equal fluxes of hydrogen and hydroxyl ions are also present in the system of weak acid and base [21].

The classic IEF is, as has been pointed out by Svensson [11] and Tiselius [12], is based upon the stationary electrolysis, which can be simply achieved by using a pure acid and base as the anolyte and

catholyte, respectively. Therefore, the data in Figs. 1 and 2 also indicate that the quasi/equal fluxes of hydrogen and hydroxyl ions are also present in the classic model of IEF, viz., Svensson's model of IEF [11].

From above data and discussions, it is evident that the quasi/equal fluxes of hydrogen and hydroxyl ions is present in the neutralization boundary formed with pure acid and base, in stationary electrolysis and in Svensson's IEF [11,12]. Apparently, these findings completely coincide with the theoretical inference—the existence of quasi/equal fluxes of hydrogen and hydroxyl ions in the stationary electrolysis on which Svensson's IEF is based, as derived in the accompanying paper [10].

Of course, research on the relationships between moving chemical reaction boundary and isoelectric focusing is not at an end. In our further studies on this subject, we will compare the experimental and theoretical velocities of ampholyte dyes in moving the neutralization reaction boundary formed by an acid and a base, coupled with or without a background electrolyte like KCl [1–4,8,9].

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References

- [1] J. Deman, W. Rigole, *J. Phys. Chem.* 74 (1970) 1122.
- [2] J. Deman, *Anal. Chem.* 42 (1970) 321.
- [3] J. Pospichal, M. Deml, P. Bocek, *J. Chromatogr.* 638 (1993) 179.
- [4] M. Deml, J. Pospichal, *Theor. Appl. Electrophoresis* 4 (1994) 107.
- [5] C.-X. Cao, *Acta Phys. Chim. Sinica* 13 (1997) 827.
- [6] C.-X. Cao, *Acta Phys. Chim. Sinica* 13 (1997) 833.
- [7] C.-X. Cao, *Acta Chem. Scand.* 813 (1998) 153.
- [8] C.-X. Cao, *J. Anhui Normal Univ.* 20 (1997) 329.
- [9] C.-X. Cao, W.-K. Chen, *Acta Chem. Scand.* (1998) (in press).
- [10] C.-X. Cao, *J. Chromatogr. A* 813 (1998) 153.
- [11] H. Svensson, *Acta Chem. Scand.* 15 (1961) 325.
- [12] A. Tiselius, *Scansk. Kem. Tidshr.* 58 (1941) 305.
- [13] C.-X. Cao (in preparation).
- [14] R.L. David (Ed.), *CRC Handbook of Chemistry and Physics*, 73rd ed., CRC Press, Boca Raton, FL, 1992–1993, p. D-167.
- [15] A.W. Adamson, *A Textbook of Physical Chemistry*, Academic Press, New York, London, 1973, pp. 489–512.
- [16] J.C. Reijenga, E. Kenndler, *J. Chromatogr. A* 659 (1994) 403.
- [17] W. Friedl, J.C. Reijenga, E. Kenndler, *J. Chromatogr. A* 709 (1995) 163.
- [18] C.-X. Cao, *J. Chromatogr. A* 771 (1997) 374.
- [19] C.-X. Cao, *J. High Resolut. Chromatogr.* 20 (1997) 701.
- [20] Z. Buzas, L.M. Hjelmeland, A. Chrambach, *Electrophoresis* 4 (1983) 27.
- [21] C.-X. Cao et al. (in preparation).