Short communication

Comparisons of the mobilities of salt ions obtained by the moving boundary method and two empirical equations in capillary electrophoresis

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Abstract

The actual mobilities of some small salt ions with high charge intensities, such as Cl^-, K^+, Na^+, Ba^{2+}, SO_4^{2-} and La^{3+}, calculated using two empirical equations., $\mu_{act} = \mu_0 \exp(-0.77\sqrt{z}I)$ [valid for $z \geq 2$ and 0.001 mol/l$\leq I \leq 0.1$ mol/l] and $\mu_{act} = \mu_0 \exp(-0.5z^{1.78}\sqrt{I})$ [valid for $I \leq 0.001$ mol/l], are compared with the actual mobilities determined by the moving boundary method (here, μ_{act} and μ_0 are the actual and absolute mobilities, respectively, z is the charge of the ion, I the ionic strength). The results show that, (i) under the given conditions both of the empirical equations are valid for small ions with high charge intensities as well as large ions with low charge intensities, (ii) the former is also valid for multivalent ions of ionic strength $I \leq 0.001$ mol/l, (iii) the latter also applies to monovalent ions of ionic strength 0.001 mol/l$\leq I \leq 0.1$ mol/l. Thus, the two equations can be expressed as a single equation: $\mu_{act} = \mu_0 \exp(-\eta\sqrt{z}I)$ [used for $I \leq 0.1$ mol/l, and if $z = 1$, $\eta = 0.5$, or if $z \geq 2$, $\eta = 0.77$].

Keywords: Moving boundary method; Electrophoretic mobility; Anions; Cations

1. Introduction

Ionic mobility is a key physicochemical property, and is of importance in zone electrophoresis, especially in capillary zone electrophoresis (CZE). Generally, there are five kinds of mobilities, absolute (μ_0), actual (μ_{act}), effective (μ_{eff}), electroosmostic (μ_{EOF}) and overall/apparent (μ_{all}) mobilities. Absolute mobility in an infinite diluted solution, viz., ionic strength being close to zero, can be obtained from the equivalent ionic conductivity extrapolated to infinite dilution solution with the formula

$$\mu_0 = \lambda_0/F \tag{1}$$

where λ_0 is the equivalent ionic conductivity in an infinite dilution solution, and F is Faraday's constant. Actual mobility is mobility of a fully protonated or deprotonated ion under a given ionic strength [1], and the formula used to obtain the actual mobility from the ionic transference number in a pure solution [2,3], is

$$\mu_{act} = \lambda T/F \tag{2}$$

where λ is the equivalent conductivity of a pure solution, T the transference number. The effective mobility is expressed by Tiselius [4] as

$$\mu_{eff} = \sum f \, a_i \, \mu_i \tag{3}$$

where μ_i is the absolute mobility of species i, a_i the fraction of species i and f the correction factor

accounting for the deviation from ideality. The electroosmostic mobility can be determined using an electroosmostic flow (EOF) marker that is uncharged under the given conditions, such as sulphanilamide and sulphaguanidine at pH 7 [5]. Overall/apparent mobility is defined by [5]

$$\mu_{all} = \mu_{eff} + \mu_{EOF} \qquad (4)$$

The actual mobility can be computed with Eq. (2) from the transference number that may be determined by Hittorf's method or the moving boundary method [2,6–8]. It may also be determined by capillary electrophoresis as has been performed by Friedl et al. [1]. Both of the methods are precise, but time-consuming and tedious.

In order to obtain ionic mobility easily, a number of papers on this subject were published. The research concerned ionic mobility as a function of pH [9], the influence of buffer concentration on ionic mobility [10,11], and the effect of ionic charge numbers and the ionic strength of the background electrolyte on mobility [1,12–14]. Among those studies, two convenient empirical equations to calculate actual mobility were formulated

$$\mu_{act} = \mu_0 \exp(-0.77 \sqrt{zI})$$

[used for $z \geq 2$ and 0.001 mol/l $\leq I \leq$ 0.1 mol/l]

$$\qquad (5)$$

$$\mu_{act} = \mu_0 \exp(-0.5 z^{1.78} \sqrt{I})$$

[used for $I \leq$ 0.001 mol/l]   (6)

As has been pointed out by Reijenga and co-workers [1,12], Eq. (5) was formulated for the mobilities of twenty-one aromatic sulfonates with low electrical charge intensities, anion charge numbers between 2 and 6 and ionic strengths in the range 0.001–0.1 mol/l, and Eq. (6) is valid for ionic strengths $I \leq 0.001$ mol/l. Are Eqs. (5,6) valid for small ions of salts with high charge intensities, such as Cl^-, K^+, Na^+, Ba^{2+}, SO_4^{2-} and La^{3+}, under the given and other conditions?

The main purpose, in this paper, is to evaluate the validity of Eqs. (5,6) for small ions of salts with high electric charge intensities under the given conditions (see Eqs. (5,6)) and other conditions as will be described in Section 3 Section 4.

2. Data and treatments

The solutions used to determine and calculate ionic mobility are KCl, NaCl, BaCl$_2$, Na$_2$SO$_4$ and LaCl$_3$, each with different concentration, viz., ionic strength, as given in Table 1.

The transference numbers, monitored by the moving boundary method, are quoted from Refs. [2,6–8]. The limited transference numbers in infinite diluted solutions are obtained from [6]

$$T_{0,\pm} = \mu_{0,\pm}/(\mu_{0,+} + \mu_{0,-}) \qquad (7)$$

where, T is the transference number, the subscripts, + and −, indicate the cation and anion, respectively, and the subscript, 0, means the transference number

Table 1
The transference numbers (T_+, T_-) of some ions in salt solutions and the equivalent conductivities ($\lambda \cdot 10^{-2}$ m^{2}S/mol) of some salt solutions at different concentrations and 25°C

Concentration (M)	KCl			NaCl		BaCl$_2$		Na$_2$SO$_4$		LaCl$_3$	
	T_+^a	T_-^a	λ	T_+	λ	T_+	λ	T_-	λ	T_+	λ
Infinite[b]	0.491	0.509	1.498	0.396	1.264	0.455	1.399	0.614	1.298	0.487	1.459
0.0005[c]	0.491	0.509	1.477	0.394	1.244	0.451	1.359	0.614	1.257	0.475	1.396
0.001[c]	0.491	0.509	1.469	0.393	1.237	0.449	1.343	0.615	1.241	0.473	1.370
0.005[c]	–	–	–	–	–	0.444	1.280	0.615	1.171	0.467	1.275
0.010	0.490	0.510	1.412	0.392	1.185	0.440	1.239	0.615	1.124	0.463	1.218
0.020	0.490	0.510	1.383	0.390	1.157	0.436[c]	1.190	0.616	1.067	–	–
0.050	0.490	0.510	1.333	0.388	1.110	–	–	–	–	–	–
0.100	0.490	0.510	1.289	0.387	1.067	–	–	–	–	–	–

[a] T_+ and T_- indicate the cation and anion transference numbers, respectively.
[b] Those transference numbers are evaluated by Eq. (7).
[c] The transference numbers are obtained from their curves (see Fig. 17 in Ref. [2]).

in an infinite dilution solution. The anion transference numbers, T_-, at different concentration are obtained with

$$T_- = 1 - T_+ \qquad (8)$$

The equivalent conductivities are quoted from Ref. [15] (see Table 1), the absolute mobilities of ions, quoted from Ref. [6], are listed as follows $(\times 10^{-8}\ m^2\ V^{-1}\ s^{-1})$: $\mu_{0,K^+} = 7.62$; $\mu_{0,Cl^-} = 7.91$; $\mu_{0,Na^+} = 5.19$; $\mu_{0,Ba^{2+}} = 6.59$; $\mu_{0,SO_4^{2-}} = 8.27$; $\mu_{0,La^{3+}} = 7.21$

The ionic strength is calculated by [1]

$$I = 0.5 \sum c_i z_i^2 \qquad (9)$$

where c_i is the concentration of species i, and z_i the charge of species i.

The exact actual mobility (μ_1), is computed using Eq. (2), and the approximate mobility is evaluated by Eq. (5) (μ_2) or Eq. (6) (μ_3). The relative difference (RD) is evaluated using

$$RD = [\mu_2\ (or\ \mu_3) - \mu_1] / \mu_1 \qquad (10)$$

In order to compute I, μ_1, μ_2, μ_3 and RD, a computer (486/DX-80, 8 Mbyte RAM, 540 Mbyte hard disk, Copam Electronics, Taiwan) was used and a simple program was written in QBASIC (ver. 4.5, Microsoft, Redmond, WA, USA). The statistical analyses of the calculated data were done with a scientific calculator (fx3600p, Casio Computer Co. LTD, Japan).

3. Results and discussions

3.1. Comparisons among μ_1, μ_2 and μ_3 for multivalent ions of salts

As shown in Fig. 1, under the conditions of ionic strength 0.001-0.1 mol/l or less than 0.001 mol/l, the correlation coefficient (CC) is 0.991 or better, a value very similar to the values of 0.995 and 0.996 obtained by Friedl et al. [1]. The RD values between μ_1 and μ_2 for Ba^{2+}, SO_4^{2-} and La^{3+} are less than 5% under the given conditions as shown in Fig. 2, and it is observed that the lower the ionic strength, the smaller the value of RD becomes. The results indicate that, (i) the correlation between the mea-
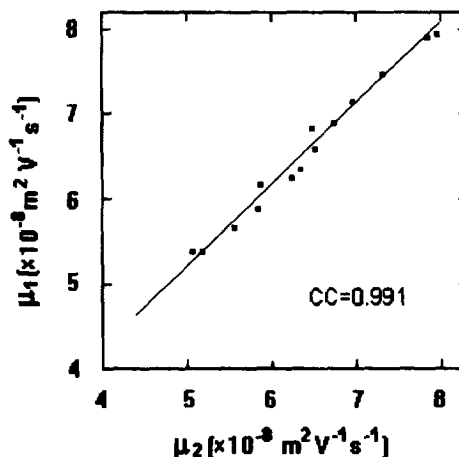

Fig. 1. The correlation between the mobility determined by the moving boundary method and that calculated by Eq. (5), viz., μ_1 and μ_2, for multivalent ions of salts of ionic strength less than 0.1 mol/l ($n = 14$).

sured mobilities (viz., Eq. (2)) and those calculated with Eq. (5) is excellent, (ii) Eq. (5) is suitable for the small ions of salts with high charge intensities as well as for large ions with low charge intensities [1], (iii) Eq. (5) is not only valid for the ionic strength range 0.001-0.1 mol/l, but also valid for ionic strength less than 0.001 mol/l.

However, the RD values between μ_1 and μ_3 are very high for the ionic strength range 0.001-0.1 mol/l, but low (less than 5%) for ionic strength less than 0.001 mol/l, as shown in Fig. 2. It is evaluated
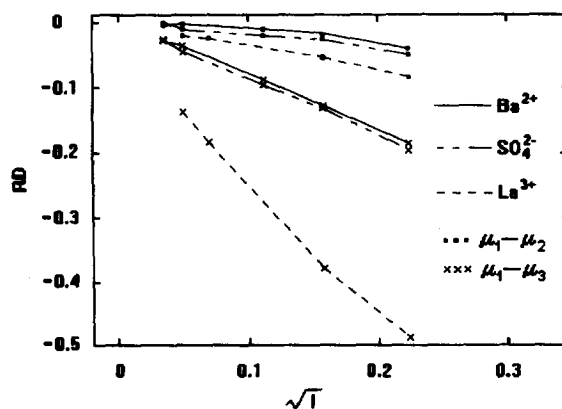

Fig. 2. The relative differences between μ_1 and μ_2 and between μ_1 and μ_3 for multivalent ions of salts of ionic strength less than 0.1 mol/l.

that the value of CC (0.849) is poor. The results show that Eq. (6) is only valid for multivalent ions of ionic strength less than 0.001 mol/l, but invalid for multivalent ions of ionic strength 0.001–0.1 mol/l. The results are in agreement with those obtained by Friedl et al. [1]. The reason that Eq. (6) is not suitable for multivalent ions of ionic strength 0.001–0.1 mol/l is, probably, that the influence of the charge number is overestimated, a theory purported by Reijenga and coworkers [1,12].

From the above discussions, clearly, Eq. (5) is valid for small multivalent ions of salts with high charge intensities as well as large multivalent ions with low charge intensities [1], if the ionic strength does not exceed 0.1 mol/l (this is different from the original ionic strength range of 0.001–0.1 mol/l, see Eq. (5)).

3.2. Comparisons of μ_1, μ_2 and μ_3 for monovalent ions of salts

The RD values for uni-univalent electrolytes are shown in Fig. 3. The CC values between μ_1 and μ_2 and between μ_1 and μ_3 in different ionic strength ranges are shown in Table 2.

The agreement between μ_1 and μ_2 of ionic strength range 0.001–0.1 mol/l is poor, and in some cases, the RD values are obviously over 5% and even close to 10% (see Fig. 3), and the CC value for μ_1 and μ_2 is 0.9873, which is lower in contrast to that for μ_1 and μ_3 (0.9988, see Table 2). The poor agreement between μ_1 and μ_2 for monovalent ions
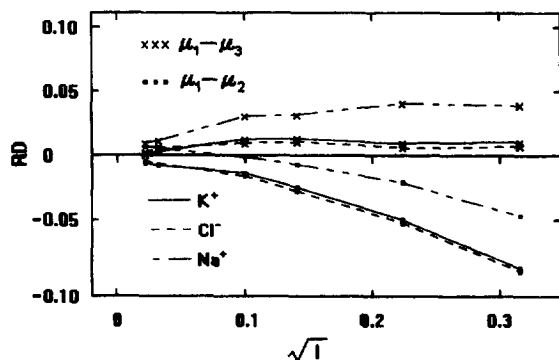

Fig. 3. The relative differences between μ_1 and μ_2 and between μ_1 and μ_3 for monovalent ions of salts of ionic strength less than 0.1 mol/l.

Table 2
The correlation coefficients (CC) between μ_1 and μ_2 and μ_1 and μ_3 for monovalent ions in different ionic strength ranges

	Infinite–0.001 mol/l	0.001–0.1 mol/l
CC between μ_1 and μ_3	0.9999	0.9988
CC between μ_1 and μ_2	0.9999	0.9873

under the given conditions is coincident with the findings of Friedl et al. [1] in which they discovered that the actual mobilities for monovalent ions determined by capillary electrophoresis are not in agreement with those calculated by Eq. (5).

However, the agreement between μ_1 and μ_3 in the same ionic strength is quite good. It is obvious from Fig. 3 and Table 2 that, (i) all of the RD values are less than 5%, (ii) the CC for μ_1 and μ_3 is 0.9988, a value very near to 1. The results show that the actual mobility calculated using Eq. (6) is almost completely coincident with that obtained from the moving boundary method in the ionic strength range 0.001–0.1 mol/l. Similar results can also be observed in other uni-univalent electrolytes like HCl [16]. The results prove that Eq. (6) is also valid for uni-univalent electrolytes even if the ionic strength is in the 0.001–0.1 mol/l range, exceeding the original range of "infinite–0.001 mol/l" [1,12].

It is interesting to note that the CC values between μ_1 and μ_2 and between μ_1 and μ_3 are excellent if the ionic strength is less than 0.001 mol/l (see Table 2), and that the RD values for both μ_1 and μ_2 and μ_1 and μ_3 are very low, in some cases almost equal to zero. The results prove that Eq. (6) is valid for the original ionic strength range of "infinite–0.001 mol/l" [1,12], and that Eq. (5) is also valid for the same ionic strength, although it is invalid for the ionic strength range of 0.001–0.1 mol/l.

Due to $z^{1.78} = \sqrt{z}$ (if $z = 1$), one may express Eq. (6) as

$$\mu_{act} = \mu_0 \exp(-0.5\sqrt{z}I)$$

(used for $z = 1$ and $I \leq 0.1$ mol/l)   (11)

which is valid for $z = 1$ and ionic strength $I \leq 0.1$ mol/l. It is also found that Eq. (11) is suitable for those monovalent ions of Cl^- in $BaCl_2$ or $LaCl_3$ and for Na^+ in Na_2SO_4, if the ionic strength does not exceed 0.1 mol/l [16].

4. Conclusion

It is clear from the discussions in Sections 3.1 and 3.2, that, (i) the empirical equations are valid for small ions of salts with high electric charge intensities as well as large ions with low charge intensities under the given conditions as mentioned in Eqs. (5,6), (ii) Eq. (5) is also valid for multivalent ions of ionic strength less than 0.001 mol/l, and (iii) Eq. (6) is also suitable for monovalent ions of ionic strength 0.001–0.1 mol/l. Thus, from Eqs. (5,11), one has following equation which is valid for mono- or multivalent ions of ionic strength less than 0.1 mol/l.

$$\mu_{act} = \mu_0 \exp(-\eta\sqrt{zI})$$

(if $z = 1$, $\eta = 0.5$ and if $z \geq 2$, $\eta = 0.77$)   (12)

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