Evaluation of weak ion association between tetraalkylammonium ions and inorganic anions in aqueous solutions by capillary zone electrophoresis

Julius Mbuna, Toshio Takayanagi, Mitsuko Oshima, Shoji Motomizu*

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan

Abstract

The evaluation of weak ion association between eleven (11) inorganic anions (charge -1 to -3) and five n-tetraalkylammonium ions, R_4N^+ (R: methyl, Me; ethyl, Et; propyl, Pr; butyl, Bu; pentyl, Am) in aqueous media at $25\,°C$ was studied. The analysis of ion association equilibria was carried out under acidic condition (formate buffer, pH 3.5) at low separating potential ($-10\,kV$) using a coated capillary with suppressed electroosmotic flow ($\mu = 4 \times 10^{-5}\,cm^2\,V^{-1}\,s^{-1}$). Direct UV detection was done at anode ($\lambda = 220\,nm$). The combination of the aforementioned conditions ensured that ion association constants, K_{ass}, between n-tetraalkylammonium ion and the small inorganic anions were reliably determined after a non-linear least squares (NLLS) treatment of the measured anion's mobility. Like their larger counterparts, small anions showed increased interaction with an increase in size of pairing ions. Moreover, for a specific cation, the interaction of small anions increased with an increase in size of the hydrated anions as reflected by the relationship between the K_{ass} and the Stokes' radius. A favourable comparison exists between the results presented in this work and those previously documented from other analytical techniques like conductometry. Qualitatively, the mobility of the anions appeared to obey the Hückel's model more closely than the more elaborate Zwanzig and Hubbard–Onsager models.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Ion association constants; Stokes' radius; Weak ion association; Tetraalkylammonium ions; Inorganic anions

1. Introduction

Capillary electrophoresis has become an established method in separation sciences with a proven ability to separate a broad spectrum of chemical species in a wide range of matrices. Capillary electrophoresis's separating ability is evident in the separation of species as diverse as isotopes [1], small inorganic anions and cations [2], organic anions [3,4] and macromolecules like carbohydrates [5] and DNA [6].

Apart from its role as a separating technique, capillary electrophoresis also finds increasing application in studies of interactions between or among chemical species and the knowledge derived is in turn used to enhance the technique's separating ability. Interactions among various proteins [7], proteins and sugars [8], and neutral species with sodium dodecyl sulphate [9] have been previously reported. Ion–ion interactions, which can be categorised as either weak or strong, are known to influence most of the capillary zone electrophoresis separations carried out on charged species. Most of the early work on ion–ion interactions was examined by conductometric methods [10,11] based on Debye–Hückel activity theory and Onsager equation [12] despite their known limitations. Another important feature of early ion–ion conductometric study was that most of the measurements were made in organic solvents because of the ease with which equilibrium constant could be determined. Alternatively, the same interactions can be investigated by capillary zone electrophoresis [13–21] which offers benefits like multi-ion, low ion concentration analysis and precise control of experimental conditions such as ionic strength, pH, etc. [14]. The basis of electrophoresis technique in interaction studies is the measurement of the mobility, which enables small changes in mobility of a given species to be accurately computed. As a result CZE is capable of studying the interactions in organic as well as aqueous media, where small changes in mobility often occur due to limited association. Studies on strong

* Corresponding author. Tel.: +81-86-251-7846;
fax: +81-86-251-7846.

E-mail address: motomizu@cc.okayama-u.ac.jp (S. Motomizu).

ion–ion interactions by CZE, involving quaternary ammonium with aromatic ions [14–18]; metal ions with crown ethers [19,20] and metal-pyridylazoresorcinolato chelates with quaternary ammonium ions, non-ionic surfactants and polyethylene glycol [21] have been previously reported. The stated interactions were investigated with the use of ordinary silica capillary by monitoring the mobility of bulky ions, which often possess low mobility and display strong interactions with the pairing ion. CZE has therefore been reliably employed in the measurement of the ion's mobility and subsequently in determination of their association constants.

Despite being thought to operate in biological fluids, natural products and pharmaceuticals, weak ion interactions have received comparatively less attention. As far as the CZE technique is concerned, the difficulty may lie in reliable determination of mobility of small anions using ordinary silica capillary since most inorganic anions possess high mobility (higher than eof) and consequently may not be detected under positive potential. Applying a negative potential will give analytes peaks but no peak for eof markers can be recorded. The use of a coated capillary with suppressed eof may overcome this problem. The aim of this work therefore, was to determine association constants, K_{ass} between the small inorganic anions and tetraalkylammonium ions in aqueous media at 25 °C, by measuring of the mobility of anions using a coated capillary. This work reports on the aforementioned weak ion association with a view of assessing the method, based on related works [14–21] and discusses the observed trends in association constants, K_{ass} and mobility of the inorganic anions.

2. Experimental

2.1. Apparatus

Hewlett Packard ^{3D}CE system (Waldbronn, Germany) equipped with diode array detector (DAD—UV detection) and fitted with a water-cooled cooling bath was used for the measurement of the electrophoretic mobility of the pairing anions. Celect N–CE-coated capillary (Supelco, Missouri, USA) of 50 μm (i.d.), 375 μm (o.d.), 40 cm (effective length) and 48.5 cm (total length) with suppressed eof ($\mu = 4 \times 10^{-5}$ cm^2 V^{-1} s^{-1}) was used for apparent mobility, μ'_{ep}, measurement. Analytical data signals processing and system control were handled by HP ^{3D}Chemstation software.

2.2. Reagents

2.2.1. Pairing cations

n-Tetraalkylammonium R$_4$N$^+$ chlorides were all purchased from Tokyo Kasei Kogyo (Tokyo, Japan). These salts were dissolved in distilled water to make stock solutions (0.25 M).

2.2.2. Pairing anions

Except for potassium ferricyanide (source of ferricyanide ions) and nitric acid (source of the nitrate ions), all the solutions containing anions were prepared from their corresponding sodium salts (thiocyanate, thiosulphate, nitrite, iodide, bromide, chromate, iodate, bromate, perrhenate). These sodium salts and the buffer solution components, formic acid/sodium formate, were all purchased from Wako Chemicals (Osaka, Japan). Distilled water was used in all solution preparations and rinsing of capillary.

2.3. Procedure

The sample solution consisted of a mixture of at least two anions (1×10^{-4} M each) and a formate buffer (5 mM, pH 3.5). The migrating solution contained the same concentration of the buffer and a variable concentration of tetraalkyl-ammonium salt (0–32 mM).

A coated capillary was consecutively flushed with distilled water and the migrating solution for 4 min. Starting with the buffer as a migrating solution, the sample was hydrodynamically introduced (50 mbar for 3 s) into the capillary and voltage applied (−10 kV). The capillary cartridge was maintained at constant temperature (25 ± 0.1 °C) and direct UV detection (220 nm) was done at anode for all the anions. After triplicate recording of migration times on electropherograms, a fresh migrating solution consisting of a buffer (5 mM) and a raised concentration of the pairing cation (tetraalkylammonium salt) was prepared and run. After a triple run, the pairing cation's concentration in the migrating solution was further raised (at regular intervals), keeping the buffer concentration constant until the operating current was about 20 μA (corresponding to ≈35 mM cation concentration). From the migration time of each pairing anion on the electropherograms, the apparent mobility, μ'_{ep}, of each anion was computed and averaged to give mobility at a particular cation concentration.

3. Results and discussion

3.1. Experimental conditions

In order to control undesirable associations, a species with possibly small hydrated radius and low charge is preferred for buffer components. Based on this criteria, formate–formic acid buffer was selected instead of citric acid–citrate or phosphoric acid–phosphate buffers. Sodium formate as a source of formate was chosen on account of sodium ion's reportedly low ability to associate with most of the anions [14,22]. It was observed that, the labelled "no eof" Celect N–CE-coated capillary, generated an eof of about 1×10^{-4} cm^2 V^{-1} s^{-1} at pH 7. To control a possible generation of electroosmotic flow in the coated capillary, acidic condition was used (buffer pH 3.5). Under this experimental pH the eof was substantially reduced to

$4 \times 10^{-5} \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$. Despite recording constant mobility of anions in the pH range 3.0–3.6, pH 3.5 was selected as it gave better precision of apparent mobility.

Total formate concentration in the buffer was kept at 5 mM during the entire analysis as it facilitated analysis of wider cation concentration range without the generation of Joule heating effect. As expected the use of 10 mM narrowed down the cation concentration range analysed.

The Ohm plot showed that voltage range from -5 to $-20 \, \text{kV}$ could be used as operating voltage without generation of the Joule heating effect and thus $-10 \, \text{kV}$ was selected. This method relies on monitoring mobility of an analyte which is likely to be affected by changes in ionic strength of the migrating solution [23]. A related work [14] has shown that mobility of most inorganic anions (nitrate, perrhenate, thiocyanate, etc.) with an exception of ferricyanide, remains constant as the ionic strength is increased up to 34 mM. The results from this report reveal that the mobility of the anions is so stable to the extent that it is not expected to change significantly beyond 34 mM. As such any decrease in mobility for most of the inorganic anions, on increasing the concentration of the pairing cation is assumed to be as a result of association. Consequently, no ionic strength-adjusting species like sodium chloride or lithium chloride was added to the migrating solution in this analysis except for ferricyanide association. For associations other than ferricyanide, the addition of an ionic strength-adjusting species in the migrating solution would nevertheless have contributed to the generation of the Joule heating effect. For all ferricyanide associations however, mobility of the ferricyanide was corrected for ionic strength effects as outlined by Motomizu and Takayanagi [14].

Since K_{ass} is derived from mobility of ions, which may be affected by ionic strength, it is reasonable to expect effects arising from ionic strength to extend to K_{ass} determination. However, the ionic strength used in this analysis ($I = 0.01$–0.04) with the corresponding activity coefficient (0.90–0.83) (by Davies equation), is likely to introduce a difference of only 0.07 in association constant K_{ass}. Accordingly, change in ionic strength is not expected to significantly affect the association constant, K_{ass} determined.

3.2. Analysis of association equilibrium

An equilibrium expression for association forming an outer-sphere complex (ion associate) between a cation C^{n+} and an anion A^{m-} can be written as:
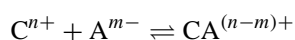
$$C^{n+} + A^{m-} \rightleftharpoons CA^{(n-m)+}$$

assuming a 1–1 association occurs at low ion pairs concentration.

The association constant, K_{ass}, can be expressed as

$$K_{\text{ass}} = \frac{[CA^{(n-m)+}]}{[C^{n+}][A^{m-}]}$$

The apparent mobility, μ'_{ep}, of an analyte ion A^{m-} can be obtained by the equation:

$$\mu'_{\text{ep}} = \frac{[A^{m-}]}{[A^{m-}] + [CA^{(n-m)+}]} \mu_A$$
$$+ \frac{[CA^{(n-m)+}]}{[A^{m-}] + [CA^{(n-m)+}]} \mu_{CA} \qquad (1)$$

where μ_A is the mobility of the anion, μ_{CA} is the mobility of the ion pair.

Taking the mass balance of A^{m-} in to account, Eq. (1) yields:

$$\mu'_{\text{ep}} = \frac{1}{1 + K_{\text{ass}}[C^{n+}]} \mu_A + \frac{K_{\text{ass}}[C^{n+}]}{1 + K_{\text{ass}}[C^{n+}]} \mu_{CA} \qquad (2)$$

Eq. (2) can be applied to 1:1 ion pairs in which the constituent ions bear different charges. However, for ions with the same charge, $\mu_{CA} \approx 0$, and therefore the apparent mobility is obtained by:

$$\mu'_{\text{ep}} = \frac{1}{1 + K_{\text{ass}}[C^{n+}]} \mu_A \qquad (3)$$

By applying a non-linear least squares (NLLS) method [18] to the treatment of mobility using an appropriate equation (Eq. (2) or Eq. (3)), the association constant, K_{ass} and simulated mobility for various pairing anions can be obtained. Figs. 1a and b and 2a and b show the effect of concentration of tetramethylammonium (Me_4N^+) and tetraamylammonium (Am_4N^+) ions on the apparent mobility of the pairing anions, respectively. The solid lines in both sets of figures represent theoretical curve fitting, which show a good agreement between the simulated and the experimentally obtained data. As shown in both sets of figures, the apparent mobility of anions decreased, to varying extents, with an increase in tetraalkylammonium ion concentration. The decrease could be attributed to the formation of neutral (for similarly charged ions) or less negatively charged ion pairs (for differently charged ion pairs), which reduce the overall apparent mobility (Eqs. (2) and (3)). A casual comparison of the two sets of figures (Figs. 1 and 2) shows a slight increase in ion association between tetraamylammonium ion with most anions despite a decrease for a few like iodate. The two sets of figures also indicate that ferricyanide interacts with the tetraalkylammonium ions most strongly, probably by virtue of its higher charge density, while bromate and iodate displayed minimum interaction. The low level of interaction shown by the iodate and bromate could be ascribed to their relatively hydrophilic nature.

Table 1 summarises log K_{ass} values obtained in the ion association between tetraalkylammonium ions and the various inorganic anions analysed in this work. It is worth noting that some of the cited values were determined in non-aqueous solvents like liquid sulphur dioxide and are therefore comparatively different. For determinations carried out in aqueous media, a favourable comparison exists
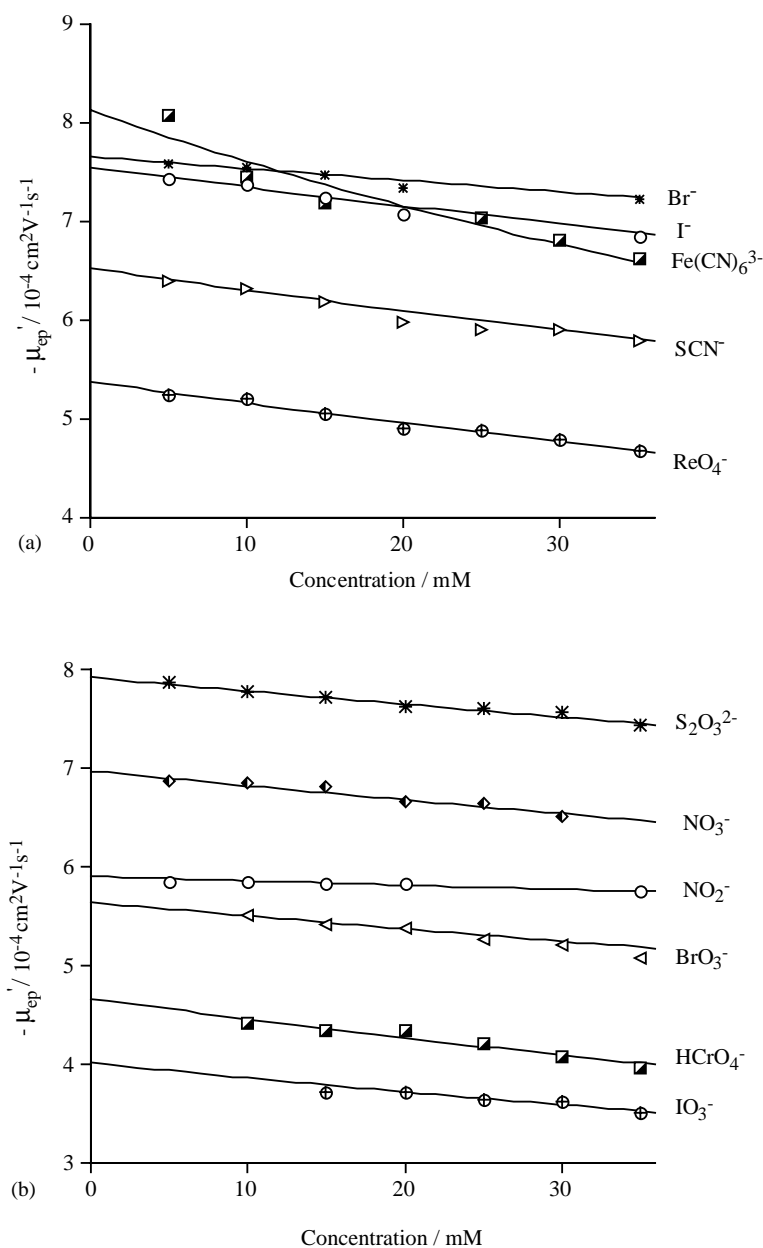
Fig. 1. (a) Effect of tetramethylylammonium ion (Me_4N^+) concentration on apparent mobility of Br^-, I^-, $Fe(CN)_6^{3-}$, SCN^- and ReO_4^-. Solid curves: theoretical curve fitting of experimental data by Eq. (2) or Eq. (3). μ'_{ep}: apparent mobility. CE conditions—sample: mixture of anions (1×10^{-4} M each); migration solution: formate buffer (5 mM) + (0–32 mM) R_4N^+; injection: 3 s at 50 mbar; applied voltage: 10 kV; capillary: coated capillary (Celect N—CE-coated capillary, eof ≈ 0); detection: 220 nm at anode. (b) Effect of tetramethylylammonium ion (Me_4N^+) concentration on apparent mobility of $S_2O_3^{2-}$, NO_2^-, NO_3^-, BrO_3^-, IO_3^- and $HCrO_4^-$. CE conditions: same as in (a).

between the results obtained in this work and the cited values [22]. The results in Table 1 also contain some abnormally small log K_{ass} values (negative log K_{ass} values), for instance the Me_4N^+–NO_2^- association constant. At the operating pH (3.5) nitrite (p$K_a = 3.2$) association is likely to be influenced by acid–base equilibrium, which may affect its complete ionisation and hence complicate its association. Similarly, chromate ion is likely to exist as a protonated species, $HCrO_4^-$ under the experimental conditions. Accordingly, its association constant more correctly

reflects association between the pairing R_4N^+ and $HCrO_4^-$ rather than R_4N^+–CrO_4^{2-} pairing.

Fig. 3a and b depict the K_{ass} trend as the alkyl group in R_4N^+ becomes increasingly bulky. Despite overlap of error bars for some K_{ass} values most anions, except for bromate, iodate and ferricyanide, showed a variable increase in the extent of interaction with the size of pairing cation. Such an observation is consistent with the previously reported findings [14,16,17] on bulky and hydrophobic organic ion association. While ferricyanide showed small fluctuations in the
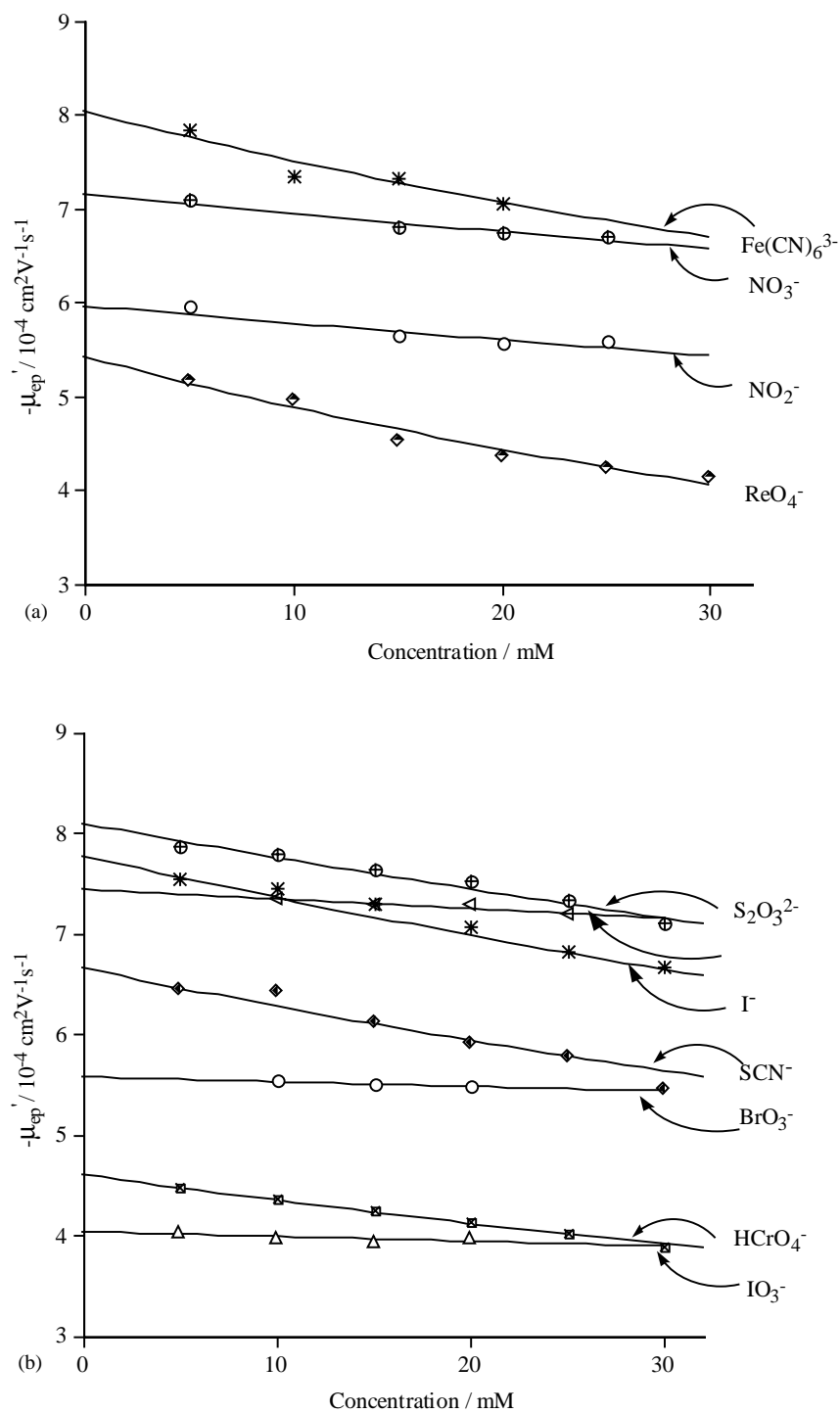
Fig. 2. (a) Effect of tetraamylammonium ion (Am_4N^+) concentration on apparent mobility of NO_3^-, $Fe(CN)_6^{3-}$, NO_2^- and ReO_4^-. CE conditions: same as in Fig. 1a. (b) Effect of tetraamylammonium ion (Am_4N^+) concentration on apparent mobility of $S_2O_3^{2-}$, Br^-, I^-, SCN^-, BrO_3^-, $HCrO_4^-$ and IO_3^-. CE conditions: same as in Fig. 1a.

level of interaction as the tetralkylammonium ion becomes more bulky, iodate and bromate showed a decreasing trend in K_{ass}. Since iodate and bromate are hydrophilic, they generally experience weak interactions with the tetralkylammonium ions. As the tetralkylammonium ion becomes bulkier

and hence more hydrophobic, their association with the two anions becomes increasingly weak.

It may also be noted that there is a break in association trend at the ethyl group (eight carbons) for a number of the anions (Fig. 3a and b). This may be explained on the basis

Table 1

Ion association constant, log K_{ass} for ion association of tetraalkylammonium ions with inorganic anions at 25 °C in aqueous solution

Anion	Cations				
	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Am_4N^+
$Fe(CN)_6^{3-}$	0.91 ± 0.3	0.91 ± 0.2	0.95 ± 0.4	0.92 ± 0.4	0.99 ± 0.4
ReO_4^-	0.63 ± 0.09	0.54 ± 0.06	0.66 ± 0.2	0.73 ± 0.07	1.05 ± 0.2
$S_2O_3^{2-}$	0.31 ± 0.04	0.37 ± 0.03	0.34 ± 0.09	0.61 ± 0.05	0.65 ± 0.05
$HCrO_4^-$	0.67 ± 0.12	0.56 ± 0.03	0.56 ± 0.06	0.64 ± 0.04	0.82 ± 0.04
I^-	0.44 ± 0.04	0.41 ± 0.02	0.50 ± 0.07	0.66 ± 0.05	0.75 ± 0.08
	$0.17^a, 0.4^a$	$0.52–0.56^a$	$0.52–0.56^a$	$0.52–0.56^a$	$0.52–0.56^a$
	0.25^b	3.15^c	$0.29–0.48^d$	$0.4–0.5^d$	0.45^e
SCN^-	0.53 ± 0.03	0.52 ± 0.12	0.67 ± 0.09	0.76 ± 0.20	0.78 ± 0.05
Br^-	0.21 ± 0.02	0.19 ± 0.02	0.19 ± 0.02	0.40 ± 0.04	0.13 ± 0.06
	0.1^a	0.24^a	0.37^a	0.44^a	2.23^f
	0.65^g	0.67^h	$-0.06–0.26^d$	0.26^h	
NO_2^-	-0.74 ± 0.09	0.50 ± 0.05	0.50 ± 0.02	0.31 ± 0.07	0.51 ± 0.2
BrO_3^-	0.40 ± 0.04	0.32 ± 0.09	0.37 ± 0.02	0.27 ± 0.04	-0.06 ± 0.01
IO_3^-	0.59 ± 0.06	0.35 ± 0.06	0.28 ± 0.02	-0.15 ± 0.01	0.09 ± 0.04
NO_3^-	0.34 ± 0.05	0.39 ± 0.01	0.39 ± 0.02	0.33 ± 0.04	0.47 ± 0.08
	3.31^i	$2.89^i, 0.8^h$	2.75^i	$0.5–0.6^a$	–

K_{ass} determined by Eq. (3), error: 3σ. Me_4N^+: tetramethylammonium ion (TMA$^+$); Et_4N^+: tetraethlyammonium ion (TEA$^+$); Pr_4N^+: tetrapropylammonium ion (TPA$^+$); Bu_4N^+: tetrabutylammonium ion (TBA$^+$); Am_4N^+: tetraamylammonium ion (TAA$^+$).

[a] In aqueous solution (conductivity data from [22] (at 25 °C)).
[b] In D_2O (conductivity data from [22] (at 25 °C)).
[c] In butanol (conductivity data from [22] (at 25 °C)).
[d] In H_2NCHO (conductivity data from [22] (at 25 °C)).
[e] In propene carbonate (conductivity data from [22] (at 25 °C)).
[f] In Me_2CO (conductivity data from [22] (at 25 °C)).
[g] In Me_2SO.
[h] In MeCN (conductivity data from [22] (at 25 °C)).
[i] In SO_2 (l) (conductivity data from [22] (at 25 °C)).

of tetraalkylammonium association with picrate ion in pure ethylene chloride and ethylidene chloride as solvents [24]. According to the study, while there is a bigger increase in contact distance between the tetraalkylammonium ion and a given anion from methyl to ethyl, only small increase in contact distance is noted in moving from ethyl to pentyl and higher homologs. Thus, there is a slight increase in size of tetralkylammonium ions from ethyl to amyl compared to that from methyl to ethyl groups in tetraalkylammonium ions. Accordingly, it is expected that the hydrated methylammonium ion will possess a significantly larger size and hence lead to slightly higher K_{ass} than ethylammonium ion.

3.3. Relationship between mobility and Stokes'/crystal radii

It is noteworthy that the mobility of nitrite and chromate ions are significantly lower than expected because the pH at which the analysis affected their complete ionisation. Consequently, these anionic species are more likely to exist in a protonated state, display diminished mobility. The mobilities of these anions will not be further discussed in relation to their crystal or Stokes' radii.

Table 2 presents the average apparent mobility (in 5 mM formate buffer solutions) of the anions studied with their corresponding crystal and Stokes' radii. As expected anions with higher charge density exhibited higher mobility than those possessing lower charge density.

Max Born proposed that ion mobility is influenced by two frictional components viz., hydrodynamic and dielectric friction, according to the expression:

$$\mu_0 = \frac{q}{f_h + f_{dl}} \tag{4}$$

where, μ_0 is the ionic mobility, q the charge, f_h the hydrodynamic friction and f_{dl} is the dielectric friction.

From their comprehensive work, Kay [27] and Hubbard and co-worker [28,29] expressed Eq. (4) as:

$$\mu_0 = \frac{ze}{6\pi\eta r_c + B' r_c^{-3}} \tag{5}$$

where z is the valency, e the electronic charge, η the viscosity, r_c the crystallographic radius and B' is the constant, such that:

$$B' = H(ze)^2 \tau \left(\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0^2} \right)$$

where τ is the relaxation time, ε_0 the low-frequency dielectric constant, ε_∞ the high-frequency dielectric constant and
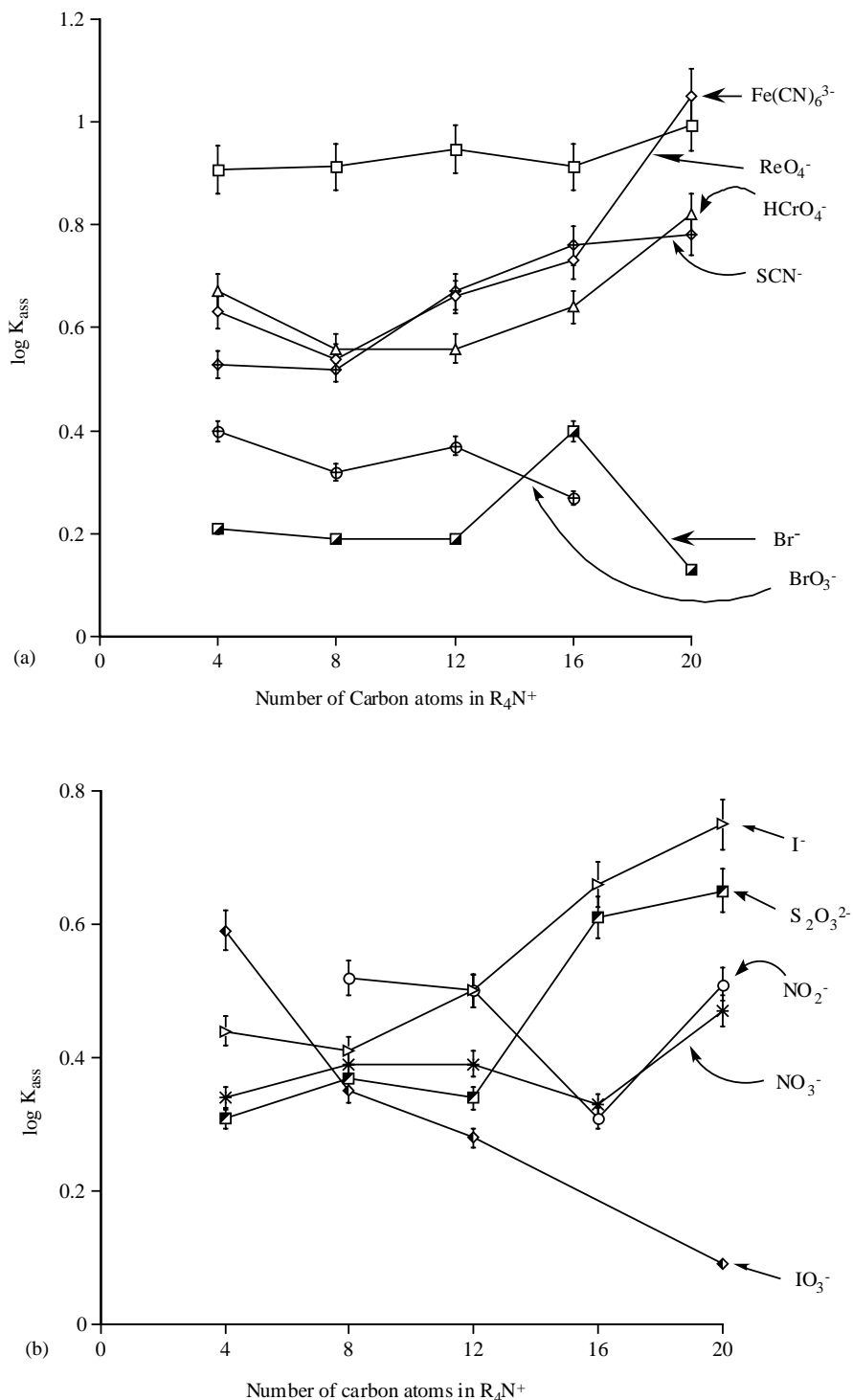
Fig. 3. (a) Variation of $\log K_{ass}$ with an increase in bulkiness of the alkyl group in tetraalkylammonium ion on associating with $Fe(CN)_6{}^{3-}$, $ReO_4{}^-$, $HCrO_4{}^-$, Br^-, SCN^- and $BrO_3{}^-$. (b) Variation of $\log K_{ass}$ with an increase in bulkiness of the alkyl group in tetraalkylammonium ion on associating with I^-, $S_2O_3{}^{2-}$, $NO_3{}^-$, $NO_2{}^-$ and $IO_3{}^-$.

H is the constant: 3/8 for Zwanzig model and 1/16.5 for Hubbard–Onsager model.

The first term in brackets in Eq. (5), denotes hydrodynamic friction coefficient, while the second term refers to the dielectric friction coefficient. Since $\varepsilon_\infty \ll \varepsilon_0$, Eq. (5) can be simplified to:

$$\mu_0 = \frac{q}{6\pi\eta r_c + H\tau q^2 \varepsilon_0^{-1} r_c^{-3}} \tag{6}$$

It can be deduced from Eq. (6) that hydrodynamic friction predominates over dielectric friction in solutions made with water as a solvent. The model further proposes that the

Table 2
Average apparent mobility of anions in pH 3.5 buffer solution and their corresponding crystal/Stokes' radii

| Anions	Ionic mobility, $-\mu$ ($\times 10^{-4}$) (cm^2 V^{-1} s^{-1})[a]	Crystal radius, r_c (Å)[b]	Stokes' radius, r_s (Å)[c]
Fe(CN)$_6^{3-}$	8.10	4.4	3.99
ReO$_4^-$	5.43	2.60	1.79
S$_2$O$_3^{2-}$	8.09	2.50	2.44
I$^-$	7.70	2.2	1.30
SCN$^-$	6.59	2.13	1.58
Br$^-$	7.74	1.96	1.25
BrO$_3^-$	5.60	1.91	1.75
IO$_3^-$	3.99	1.81	2.60
NO$_3^-$	7.14	1.79	1.40

[a] Data from this work obtained by Eq. (3), error: 3σ.
[b] Cited from [25].
[c] Cited from [26].

magnitude of dielectric friction is a function of both charge and crystal radius of the anion, albeit to different extents: charge prevails over radius. The Hubbard–Onsager model with various modifications based on Pitts equation, has been reported to successfully predict mobility at infinite dilution for organic anions like monoamines; aliphatic carboxylates and amines; and aromatic carboxylates [30–32] in aqueous solution.

Qualitatively, Zwanzig and Hubbard–Onsager model may account for mobility trend shown by the singly charged anions (Fig. 4). However, unless modified to incorporate shape parameter or dielectric friction assumed to be negligible, the model faces difficulties in explaining the high mobility shown by the nitrate ion. It is similarly challenging to account for higher mobility of Br$^-$ over SCN$^-$. Probably the water structure around ions, initially proposed by

Frank–Wen [33] may account for such a phenomena, i.e. I$^-$, Br$^-$, NO$_3^-$ classified as "water structure breaking" ions migrate more easily under applied potential. If the mobility of the nitrite and chromate ions had not been affected by the operating pH, it would have been possible to assess the dielectric friction effect, which explains the general trends expected for spherical ions [34] and significant deviations expected of non-spherical ions.

The elaborate Hubbard–Onsager model used by Lucy [34] asserts that mobility of ions is intrinsically governed by crystal radius. As suggested by the same author this assertion may apply to carboxylates and amines examined under that study. As expected for the inorganic anions analysed in this work, a linear relationship between mobility and size emerges on plotting anion's mobility versus Stokes' radius^{-1} (Fig. 5). Fig. 5 is consistent with Hückel model as
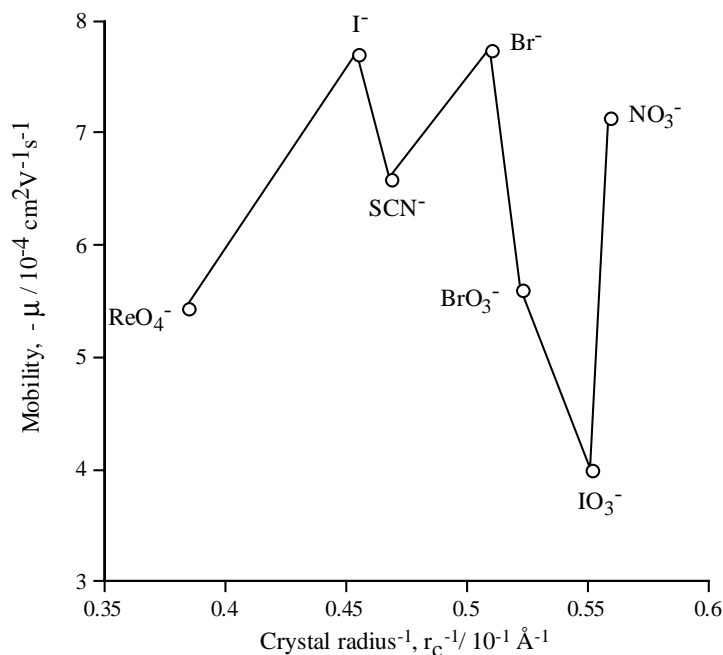
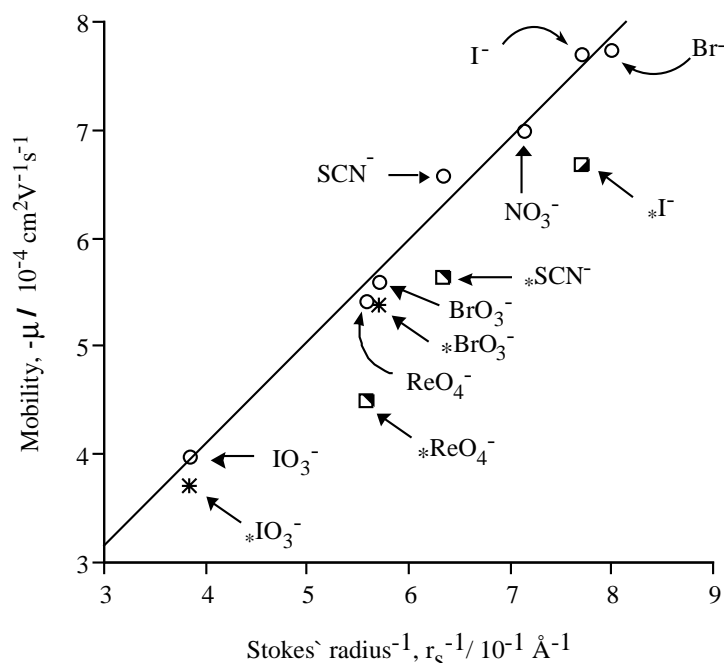Fig. 4. Relationship between anion's mobility, μ with their crystal radii.

Fig. 5. Influence of Stokes' radius of anions on their mobility. $_*IO_3^-$, $_*BrO_3^-$, $_*SCN^-$, $_*I^-$, $_*ReO_3^-$: mobility of the respective anions on adding 30 mM TBA$^+$ in migrating solution.

represented by Eq. (7).

$$\mu_0 = \frac{q}{6\pi\eta r_s} \tag{7}$$

where r_s is the Stokes' radius.

Fig. 5 can be used to quickly assess both the validity of the measured anion's mobility and significance of ion association upon introduction of an additive to migrating solution. A major deviation of measured mobility above the line may be an indication of invalidity of the data determined under the same experimental conditions. To assess whether association was important in a given analysis, use is made of the extent of deviation of mobility from the line. For weak association, addition of pairing cation to the migrating solution will result into a slight deviation of the measured mobility from the line. On the other hand, for comparatively stronger association, addition of the same concentration of cation to the migrating solution will produce relatively significant deviation from the line. As illustrated in Fig. 5 perrhenate, thiocyanate and iodide ions displayed marked deviation from the line on adding 30 mM TBA$^+$ to the migrating solution, indicating that association was significant. A similar addition of TBA$^+$ to the migrating solution only resulted into a minor deviation on mobility of iodate and bromate, indicating that association was not as important as in nitrate and perrhenate associations.

ciation comprising of small inorganic anions in aqueous solution. The K_{ass} values determined are comparable to published results determined by conductometry. There are some similarities between association involving small inorganic anions and the relatively larger organic anions. For instance the extent to which small inorganic anions associate is proportional to their charge and size of the pairing cation. According to this evaluation, no simple relationship between size of inorganic anions and association constants is apparent emphasising the complex nature inherent in ionic interactions under multi-ion electrolyte environment. Qualitatively, the mobility of anions studied appears to follow the Hückel's model more closely than the more advanced Hubbard–Onsager model. The method evaluated can be applied to assess whether ion association is significant upon introduction of an additive to migrating solution. The size of deviation of measured mobility from a line on a graph of mobility versus Stokes' radius^{-1} of anions is an indication of the importance of ion association.

4. Conclusion

The results presented in this work show that the method evaluated can be applied for analysis of weak ion asso-

References

[1] C.A. Lucy, T.L. McDonald, Anal. Chem. 67 (1995) 1074.
[2] W.R. Jones, P. Jandik, J. Chromatogr. 546 (1991) 445.

[3] A.G. Peterson, E.S. Ahuja, J.P. Foley, J. Chromatogr. A 683 (1996) 15.

[4] K.D. Altria, J. Chromatogr. A 844 (1999) 371.

[5] A. D'Hulst, N. Verbeke, J. Chromatogr. 608 (1992) 275.

[6] A. Guttman, N. Cooke, Anal. Chem. 64 (1992) 2348.

[7] F. Gomez, Z.L. Avilla, Y.-H. Chu, M.G. Whitesides, Anal. Chem. 66 (1994) 1785.

[8] S. Honda, A. Taga, K. Suzuki, K. Kakehi, J. Chromatogr. 597 (1992) 377.

[9] K.L. Rundlett, D.W. Armstrong, J. Chromatogr. A 721 (1996) 173.

[10] C.W. Davies, Trans. Faraday Soc. 23 (1927) 351.

[11] R.M. Fuoss, D. Edelson, J. Am. Chem. Soc. 73 (1951) 269.

[12] H.S. Harned, B.B. Owen, Physical Chemistry of Electrolyte Solutions, Reinhold, New York, 1964, p. 70.

[13] C.A. Chang, C.Y. Chen, H.Y. Chen, J. Chin. Chem. Soc. 46 (4) (1999) 519.

[14] S. Motomizu, T. Takayanagi, J. Chromatogr. A 853 (1999) 63.

[15] T. Takayanagi, S. Motomizu, Chem. Lett. (1995) 593.

[16] T. Takayanagi, E. Wada, S. Motomizu, Analyst 122 (1997) 57.

[17] T. Takayanagi, E. Wada, S. Motomizu, Analyst 122 (1997) 1387.

[18] T. Takayanagi, H. Tanaka, S. Motomizu, Anal. Sci. 13 (1997) 11.

[19] T. Takayanagi, T. Iwachido, S. Motomizu, Bull. Chem. Soc. Jpn. 71 (1998) 1373.

[20] L.C. Manege, T. Takayanagi, M. Oshima, T. Iwachido, S. Motomizu, Bull. Chem. Soc. Jpn. 72 (1999) 1301.

[21] T. Takayanagi, S. Motomizu, Anal. Sci. 18 (2002) 1021.

[22] E. Hogfeldt, Stability Constants of Metal–Ion Complexes (Part A), Pergamon Press, Oxford, 1982, p. 187.

[23] D. Li, S. Fu, C.A. Lucy, Anal. Chem. 71 (1999) 687.

[24] K.H. Stern, F. Healey, A.E. Martell, J. Chem. Phys. 19 (1951) 1114.

[25] Y. Marcus, Ion Properties (Table 13), Marcel Dekker, New York, 1997.

[26] Y. Kiso, Topics Surrounding Zone Electrophoresis-Ionic Processes through Matrices, Nankodo, Tokyo, 1972 (Chapter 2).

[27] R.L. Kay, Pure Appl. Chem. 63 (1991) 1393.

[28] J.B. Hubbard, L. Onsager, J. Chem. Phys. 67 (1978) 4850.

[29] J.B. Hubbard, J. Chem. Phys. 68 (1978) 1649.

[30] S. Fu, C.A. Lucy, Anal. Chem. 70 (1998) 173.

[31] S. Fu, D. Li, C.A. Lucy, Analyst 123 (1998) 1487.

[32] D. Li, C.A. Lucy, Anal. Chem. 73 (2001) 1324.

[33] H.S. Frank, W.Y. Wen, Discuss. Faraday Soc. 24 (1957) 133.

[34] C.A. Lucy, J. Chromatogr. A 850 (1999) 319.