# Internal Cation Mobilities in Molten (Na, Ag)$NO_3$ Remeasured by the Column Method

Kazunori Ichioka and Isao Okada

Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta,
Midori-ku, Yokohama 227, Japan

Alfred Klemm

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), 6500 Mainz, BRD

Z. Naturforsch. **44a**, 747–750 (1989); received June 27, 1989

Internal mobility ratios $b_{Na}/b_{Ag}$ in molten (Na, Ag)$NO_3$ have been measured with the column-method. From these, the densities and conductivities the internal mobilities have been calculated. Contrary to results obtained with other methods, over the investigated range of concentration and temperature, $b_{Ag}$ is greater than $b_{Na}$. The various methods are discussed.

## Introduction

The molar volume of molten NaX is appreciably greater than that of molten AgX ($X = NO_3$ [1, 2], X = Cl [3], X = Br [4], X = I [4]), whereas the ionic radius of $Na^+$ is slightly smaller than that of $Ag^+$ [5]. Evidently the interaction of an Ag-X pair is stronger than that of an Na-X pair, the polarizability of $Ag^+$ being much greater than that of $Na^+$. The internal mobility of $Ag^+$ in molten $AgNO_3$, however, is greater than that of $Na^+$ in molten $NaNO_3$.

The ionic mobilities in molten (Na, Ag)$NO_3$ have already been measured by five groups using different methods [6–10]. The agreement among their results is, however, poor, which prevents a fruitful discussion.

The column method [11] was originally invented for enriching isotopes and thus enables one to measure very small relative differences in internal mobilities of two isotopic ions. With LiCl at the cathode to prevent the formation of silver dendrites, the method was applied to enrich $^{107}$Ag in molten AgCl [12].

We have previously improved the column method for nitrate systems by using molten $NH_4NO_3$ in the cathode compartment [13, 14]; this enabled us to study molten nitrates containing $Ag^+$ without any problems with dendrites.

In the present work we have remeasured the internal mobilities of molten (Na, Ag)$NO_3$ by the column method.

## Experimental

The electromigration cell was of the type used in [14, 15]. The catholyte was molten $NH_4NO_3$. The large vessel, in which the separation tube was inserted, contained a molten mixture of (Li, Na, K)$NO_3$ (30-17-53 mol%), so that a low temperature range could be covered. The separation tube of Vycor of 4 mm in internal diameter was packed with alumina (150–180 μm) over ca. 200 mm from the bottom and was filled with the anolyte, a mixture of $NaNO_3$ and $AgNO_3$ of the desired composition. The chemicals $NaNO_3$ and $AgNO_3$ of reagent grade were melted and dehydrated in a small vessel by bubbling dry Ar gas before use. The small vessel was shielded from light, kept at relatively low temperature, and the mixture was used within a few days. No decomposition of $AgNO_3$ was detected throughout the experiment.

The temperature of the separation tube could be kept constant within ±1 K with a temperature controller. After a few hours of electromigration at a constant current, the separation tube was taken out and cut into pieces of 10–15 mm length. The content of $Na^+$ and $Ag^+$ was analysed by flame spectrophotometry and atomic absorption spectrophotometry, respectively. Since $Ag^+$ was apt to be adsorbed on the glass wall and the diaphragm material in neutral solution, the pieces were dipped in diluted nitric acid solution for 2 hr. The alumina powder was separated by a G-3 glass filter washed beforehand with diluted nitric acid solution. Each portion was first diluted to 100 $cm^3$. Then, 2–5 $cm^3$ in accordance with the approximate concentration of each portion was further

---

Reprint requests to Professor I. Okada, Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Midori-ku, Yokohama 227, Japan.

0932-0784 / 89 / 0800-0747 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. The relative difference in the internal mobilities. The errors given are those due to the chemical analysis.

| $T$/K | $x_{Ag}$ | $Q$/C | $\varepsilon_{NaAg}$ |
|---|---|---|---|
| 543 | 0.551 ± 0.002 | 2039 | −0.098 ± 0.001 |
| | 0.746 ± 0.003 | 2491 | −0.101 ± 0.003 |
| | 0.904 ± 0.002 | 2036 | −0.138 ± 0.004 |
| 563 | 0.321 ± 0.002 | 1308 | −0.124 ± 0.003 |
| | 0.487 ± 0.003 | 1666 | −0.139 ± 0.004 |
| | 0.716 ± 0.003 | 2517 | −0.146 ± 0.004 |
| | 0.874 ± 0.004 | 1176 | −0.166 ± 0.016 |
| 583 | 0.127 ± 0.001 | 2540 | −0.058 ± 0.002 |
| | 0.332 ± 0.004 | 2419 | −0.064 ± 0.006 |
| | 0.426 ± 0.003 | 1756 | −0.075 ± 0.002 |
| | 0.688 ± 0.002 | 2633 | −0.085 ± 0.002 |
| | 0.896 ± 0.003 | 2075 | −0.103 ± 0.005 |
| 603 | 0.119 ± 0.001 | 2642 | −0.053 ± 0.002 |
| | 0.322 ± 0.003 | 2309 | −0.067 ± 0.005 |
| | 0.589 ± 0.003 | 1815 | −0.065 ± 0.003 |
| | 0.675 ± 0.002 | 2552 | −0.072 ± 0.001 |
| | 0.900 ± 0.002 | 2077 | −0.084 ± 0.005 |
| 623 | 0.130 ± 0.001 | 2490 | −0.040 ± 0.001 |
| | 0.301 ± 0.001 | 1309 | −0.081 ± 0.002 |
| | 0.504 ± 0.002 | 1249 | −0.094 ± 0.003 |
| | 0.696 ± 0.003 | 1297 | −0.101 ± 0.004 |
| | 0.894 ± 0.005 | 1206 | −0.092 ± 0.014 |

Table 2. Internal mobilities $b_{Na}$ and $b_{Ag}$. The errors given are those due to the chemical analysis only.

| $x_{Ag}$ | $T$ (K) | $\varkappa$ ($S\,m^{-1}$) | $V$ ($10^{-6}\,m^3 \cdot mol^{-1}$) | $b_{Na}$ ($10^{-8}\,m^2\,V^{-1}\,s^{-1}$) | $b_{Ag}$ ($10^{-8}\,m^2\,V^{-1}\,s^{-1}$) |
|---|---|---|---|---|---|
| 0 | 543 | 0.792 | 43.59 | 3.58 | – |
| 0.551 | | 0.851 | 43.72 | 3.65 ± 0.00 | 4.03 ± 0.00 |
| 0.746 | | 0.880 | 43.65 | 3.68 ± 0.01 | 4.08 ± 0.00 |
| 0.904 | | 0.904 | 43.54 | 3.57 ± 0.02 | 4.13 ± 0.00 |
| 1 | | 0.918 | 43.49 | – | 4.14 |
| 0 | 563 | 0.886 | 43.92 | 4.03 | – |
| 0.321 | | 0.911 | 44.09 | 3.99 ± 0.00 | 4.51 ± 0.01 |
| 0.487 | | 0.933 | 44.05 | 3.97 ± 0.01 | 4.56 ± 0.01 |
| 0.716 | | 0.965 | 43.93 | 3.93 ± 0.01 | 4.57 ± 0.01 |
| 0.874 | | 0.986 | 43.83 | 3.83 ± 0.07 | 4.57 ± 0.01 |
| 1 | | 1.003 | 43.74 | – | 4.55 |
| 0 | 583 | 0.979 | 44.27 | 4.49 | – |
| 0.127 | | 0.986 | 44.36 | 4.50 ± 0.00 | 4.76 ± 0.01 |
| 0.332 | | 1.005 | 44.42 | 4.53 ± 0.01 | 4.83 ± 0.02 |
| 0.426 | | 1.015 | 44.39 | 4.52 ± 0.01 | 4.87 ± 0.01 |
| 0.688 | | 1.047 | 44.26 | 4.52 ± 0.01 | 4.93 ± 0.00 |
| 0.894 | | 1.073 | 44.08 | 4.45 ± 0.02 | 4.95 ± 0.00 |
| 1 | | 1.084 | 43.99 | – | 4.95 |
| 0 | 603 | 1.073 | 44.62 | 4.96 | – |
| 0.119 | | 1.076 | 44.69 | 4.95 ± 0.00 | 5.21 ± 0.01 |
| 0.322 | | 1.092 | 44.73 | 4.95 ± 0.01 | 5.29 ± 0.02 |
| 0.589 | | 1.120 | 44.62 | 4.98 ± 0.01 | 5.32 ± 0.01 |
| 0.675 | | 1.129 | 44.55 | 4.96 ± 0.01 | 5.33 ± 0.00 |
| 0.900 | | 1.153 | 44.35 | 4.90 ± 0.02 | 5.34 ± 0.00 |
| 1 | | 1.164 | 44.24 | – | 5.34 |
| 0 | 623 | 1.165 | 44.95 | 5.43 | – |
| 0.130 | | 1.168 | 45.06 | 5.42 ± 0.00 | 5.64 ± 0.01 |
| 0.301 | | 1.176 | 45.08 | 5.36 ± 0.00 | 5.80 ± 0.00 |
| 0.504 | | 1.194 | 44.99 | 5.31 ± 0.01 | 5.83 ± 0.01 |
| 0.696 | | 1.212 | 44.84 | 5.23 ± 0.02 | 5.80 ± 0.01 |
| 0.849 | | 1.228 | 44.63 | 5.21 ± 0.07 | 5.74 ± 0.01 |
| 1 | | 1.238 | 44.49 | – | 5.71 |

diluted to 100 $cm^3$ for the spectrophotometric analysis. The concentration of nitric acid in the solution for the analysis was ca. 0.16 mol $dm^{-3}$ for the samples with $x_{Ag} > 0.5$ and ca. 0.14 mol $dm^{-3}$ for $x_{Ag} < 0.5$ ($x_{Ag}$: mole fraction of Ag).

## Results

Relative differences in the internal mobilities $b$ are defined as

$$\varepsilon_{NaAg} = (b_{Na} - b_{Ag})/\bar{b}, \tag{1}$$

where $\bar{b} = x_{Na}\, b_{Na} + x_{Ag}\, b_{Ag}$. The $\varepsilon$ values, given in Table 1, have been calculated from [15]

$$\varepsilon_{NaAg} = (F/Q)\,(x_{Na}\, N_{Ag} - x_{Ag}\, N_{Na})/x_{Na}\, x_{Ag}, \tag{2}$$

where $Q$ is the transported charge, $F$ the Faraday constant, $x_{Ag}$ and $x_{Na}$ are the original mole fractions ($x_{Ag} + x_{Na} = 1$), and $N_{Na}$ and $N_{Ag}$ are the molar quantities of $Na^+$ and $Ag^+$ in the anolyte after electrolysis; in the present case the anolyte refers to the salt from the anode to the fraction where the initial composition remained unchanged.

The internal mobilities of $Na^+$ and $Ag^+$, given in Table 2, are calculated from the $\varepsilon$ values and data on the conductivities [1] and densities [1] by

$$b_{Na} = (\varkappa V/F)\,(1 + x_{Ag}\, \varepsilon_{NaAg}), \tag{3a}$$

$$b_{Ag} = (\varkappa V/F)\,(1 - x_{Na}\, \varepsilon_{NaAg}), \tag{3b}$$

where $\varkappa$ is the conductivity and $V$ the molar volume of the mixture.

The molar volumes of the present system at 543 K, 583 K and 623 K, calculated from the density measurements of Brillant [1], are shown in Figure 1. If the values recommended in [2] were adopted, the molar volume of (Na, Ag)$NO_3$ would decrease linearly with $x_{Ag}$.

The obtained isotherms of $b_{Na}$ and $b_{Ag}$ at 543 K, 583 K, and 623 K are shown in Figure 2.

## Comparison with the Results by Other Methods

The isotherms at 573 K obtained with the EMF method by Richter and Amkreutz [9] and with the Hittorf method by Connan [10] are shown in Figure 3. A comparison of Fig. 2 with Fig. 3 reveals that our results are essentially different from theirs.

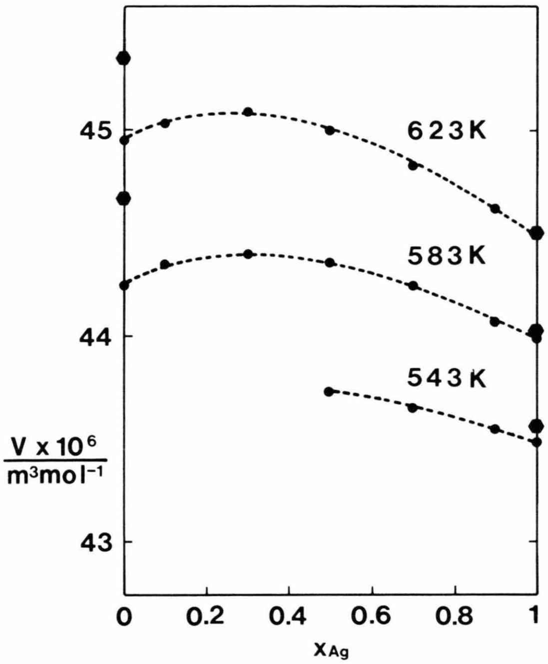

Fig. 1. The isotherms of the molar volumes based on [1]. The values for the pure melts obtained from the recommended values [2] are also shown for comparison (●).

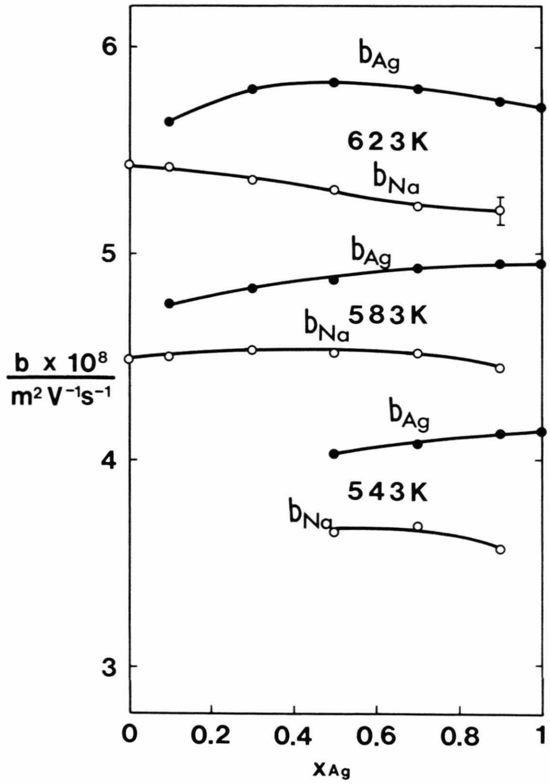

Fig. 2. Isotherms of $b_{Na}$ and $b_{Ag}$ at 543 K, 583 K, and 623 K.

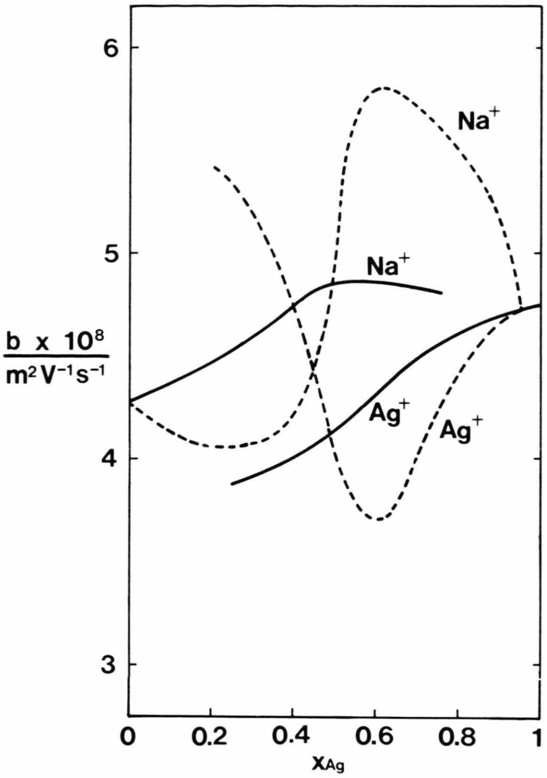

Fig. 3. The isotherms of the internal mobilities at 573 K obtained by other methods. (– –): EMF method [9], (——): Hittorf method [10]; in the latter study the external mobilities were measured, from which the internal ones are obtained.

Aziz and Wetmore [6] applied the Hittorf method with a silver anode and evaluated a function

$$\phi = (F/Q)\,(x_{Na}\,N_{Ag} - x_{Ag}\,N_{Na}) \tag{4}$$

from the data obtained for the anode compartment. Since during electrolysis $Ag^+$ ions were produced at the anode while in our case the anode was inert, for a comparison of their $\phi$ values with our $\varepsilon$ values, given by (2), $N_{Ag}$ in (4) has to be replaced by $N_{Ag} - Q/F$. One thus has

$$\varepsilon_{NaAg} = (\phi - x_{Na})/x_{Na}\,x_{Ag}\,. \tag{5}$$

The $\varepsilon$ values obtained by (5) from their $\phi$ values differ much from those in the present study, though there is qualitative agreement.

Similar experiments were performed at 578 K by Duke, Laity, and Owens [7]. From their four $\phi$ values one finds, using (5), $\varepsilon_{NaAg} = 0.37$, $-0.05$, 0.00 and 0.05 for $x_{Ag} = 0.09$, 0.30, 0.50 and 0.71, respectively. With the exception of the $\varepsilon$ value for $x_{Ag} = 0.30$, these $\varepsilon$ values are far from those given in Table 1.

Hittorf type experiments of this kind may be unrelieable for three reasons:

1. The necessary region (not point!) of unchanged composition between the cathode and anode compartments probably does not exist, the separating membrane (plug) being too thin (short).
2. The voluminous anode compartment prevents large changes in composition.
3. The production of $AgNO_3$ at the anode may be incomplete, gas being produced.

The EMF measurements of Richter and Amkreutz [9] were performed with a cell consisting of two electrode compartments connected by a liquid junction, each compartment containing a silver electrode and molten (Na, Ag)$NO_3$, the mole fractions of $AgNO_3$ in the compartments differing by $dx_{Ag}$, i.e. the chemical potentials differing by $d\mu_{AgNO_3}$. This brings about an EMF($= d\phi_B$) of the cell which is given by [16]

$$F\,d\phi_B = (1 + x_{Ag}\,\varepsilon_{NaAg})\,d\mu_{AgNO_3}. \tag{6}$$

Evidently only the small deviation of $F\,d\phi_B/d\mu_{AgNO_3}$ from unity yields the information about $\varepsilon$. This is a weakness of this method.

If, instead of silver electrodes, inert electrodes surrounded by nitrous gas would have been used, as had been done in [17] for molten (K, Ag)$NO_3$, an EMF($= d\phi_A$) given by [16]

$$F\,d\phi_A = x_{Ag}\,\varepsilon_{NaAg}\,d\mu_{AgNO_3}. \tag{7}$$

would have been obtained. This, of course, would have allowed for more precise measurements of $\varepsilon$. $\phi_A$ is the so called diffusion potential.

Although the zone electromigration method, in which radioisotopes or enriched stable isotopes have to be used, has not been applied to the present system, this method will be inferior to the column method for internal mobility ratio measurements.

Thus, the column method is superior to other methods particularly in such a system as the present one, where the difference in the mobilities of the two cations is small.

Results on the isotherms of the internal cation mobilities in the systems (Li, Ag)$NO_3$ and (K, Ag)$NO_3$ remeasured by the column method will be reported soon, and a discussion of the mobilities in the three systems (Li, Ag)$NO_3$, (Na, Ag)$NO_3$ and (K, Ag)$NO_3$ is therefore postponed.

[1] S. Brillant, Thesis, Strasbourg 1967.
[2] G. J. Janz, U. Krebs, H. F. Siegenthaler, and R. P. T. Tomkins, J. Phys. Chem. Ref. Data **1**, 581 (1972).
[3] A. Krekelberg, W. Merkens, and J. Richter, Z. Naturforsch. **38a**, 890 (1983).
[4] E. Bossmann, M. Müller, and J. Richter, Z. Naturforsch. **42a**, 426 (1987).
[5] R. D. Shannon, Acta Cryst. **A32**, 751 (1976).
[6] P. M. Aziz and F. E. W. Wetmore, Can. J. Chem. **30**, 779 (1952).
[7] F. R. Duke, R. W. Laity, and B. Owens, J. Electrochem. Soc. **104**, 299 (1957); R. W. Laity, J. Amer. Chem. Soc. **79**, 1849 (1957).
[8] M. Lorentz and G. J. Janz, J. Phys. Chem. **61**, 1683 (1957).
[9] J. Richter and E. Amkreutz, Z. Naturforsch. **27a**, 280 (1972).
[10] R. Connan, J. Chim. Phys. **70**, 888 (1973).
[11] A. Klemm, H. Hintenberger, and P. Hoernes, Z. Naturforsch. **2a**, 245 (1947).
[12] S. Floberg, A. Klemm, and C. Lang, Z. Naturforsch. **8a**, 562 (1953).
[13] I. Okada and N. Saito, J. Nucl. Sci. Technol. **11**, 314 (1974).
[14] I. Okada, Z. Naturforsch. **33a**, 498 (1978).
[15] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34a**, 498 (1979).
[16] cf. e.g. A. Klemm in "Advances in Molten Salt Chemistry", Vol. 6, p. 45 (G. Mamantov, C. B. Mamantov, and J. Braunstein, eds.), Elsevier 1987.
[17] M. Okada and K. Kawamura, Electrochim. Acta **15**, 1 (1970).