Internal Cation Mobilities in the Molten Systems (Ag, Rb)NO_3 and (Ag, Cs)NO_3 Remeasured by the Klemm Method

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Internal mobility ratios in the molten binary systems (Ag, Rb)NO_3 and (Ag, Cs)NO_3 have been measured by Klemm's countercurrent electromigration method at various temperatures and compositions. From these and the available data on the densities and conductivities, the cation internal mobilities b have been calculated. Over the investigated regions of temperature and composition b_{Ag} is greater than b_{Rb} and b_{Cs}. The internal mobility of Ag^+ is well expressed by $b_{Ag} = [A/(V - V_0)] \cdot \exp(-E/RT)$, where V is the molar volume of the mixtures, A, V_0, and E being constants nearly independent of the coions. A comparison of the present data with those previously obtained by the EMF method certifies that the Klemm method yields more precise data.

Introduction

In previous studies the relative differences in internal cation mobilities in the molten binary systems (Ag, M)NO_3 (M = Li [1], Na [2], and K [1]) have been measured by Klemm's countercurrent electromigration method, and from these and the available data [3] on the densities and conductivities the internal cation mobilities have been calculated. A comparison of these data with those obtained by the EMF and Hittorf method has shown [1, 2] that the Klemm method yields the most precise internal mobilities among the available methods.

For the systems (Ag, Rb)NO_3 and (Ag, Cs)NO_3, the internal mobilities have been measured by the EMF (A) and EMF (B) methods for the former [4, 5], and by the EMF (B) method for the latter system [5]. In the present study we have remeasured these mobilities by the Klemm method and compared the results with those obtained by the EMF methods. Here, the EMF (A) and (B) methods are defined as the ones which employ the following types of cells [6]:

Type A:

$$(Pt)\,NO_2,\ O_2\,|\,AgNO_3,\ MNO_3(I)\,\|\,AgNO_3,\ MNO_3(II)\,|\,NO_2,\ O_2\,(Pt) \qquad (1)$$

Type B:

$$Ag\,|\,AgNO_3,\ MNO_3(I)\,\|\,AgNO_3,\ MNO_3(II)\,|\,Ag, \qquad (2)$$

where M is alkali metal ion and the concentrations of Ag and M are different in compartments (I) and (II), between which a liquid junction potential is generated.

The present data are also compared with those measured for other silver nitrate-alkali nitrate systems by the Klemm method.

Experimental

$AgNO_3$, $RbNO_3$ and $CsNO_3$ of reagent grade made by Wako Chem. Co. Ltd., Japan, were used. These salts were vacuum-dried at 453 K for two days. The electromigration cell was of the type used in [7]. As the catholyte, molten NH_4NO_3 was used. The large vessel of the cell, in which the separation tube was set, contained a molten ternary mixture of (Li, Na, K)NO_3 (30–17–53 mol%). The separation tube of Vycor of 4 mm in internal diameter was packed with silica powder (150–180 μm). Constant electric current of 80 mA was supplied for the electromigration. The experimental procedure was similar to that employed in the previous study [2]. The content of Ag, Rb and Cs was analysed by atomic absorption spectrophotometry.

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Table 1. Relative differences in the internal mobilities in (Ag, Rb)NO_3 (the errors in ε are due to only the chemical analysis) and corresponding internal mobilities b_{Ag} and b_{Rb}.

T/K	x_{Rb}	Q/C	ε	$\varkappa$ (10^2 S m^{-1})	V (10^{-6} m^3 mol^{-1})	b_{Ag} (10^{-8} m^2 V^{-1} s^{-1})	b_{Rb}
523	0	---	---	0.8285	43.32	3.791	---
	0.048 ± 0.000	1186	0.150 ± 0.004	0.7832	43.98	3.596 ± 0.008	3.057 ± 0.015
	0.101 ± 0.001	1198	0.154 ± 0.004	0.7380	44.71	3.473 ± 0.001	2.945 ± 0.015
	0.285 ± 0.001	1303	0.179 ± 0.003	0.5935	47.30	3.059 ± 0.002	2.535 ± 0.006
	0.467 ± 0.001	1203	0.177 ± 0.001	0.4771	49.90	2.673 ± 0.002	2.234 ± 0.002
	0.673 ± 0.002	1195	0.173 ± 0.002	0.3746	52.81	2.290 ± 0.003	1.934 ± 0.001
	0.820 ± 0.000	1189	0.160 ± 0.001	0.3138	54.79	2.017 ± 0.002	1.730 ± 0.000
	1	---	---	0.2406[a]	57.02[a]	---	1.421[a]
543	0	---	---	0.9123	43.55	4.117	---
	0.055 ± 0.001	1213	0.163 ± 0.006	0.8642	43.91	3.967 ± 0.001	3.327 ± 0.024
	0.098 ± 0.001	1159	0.171 ± 0.004	0.8162	44.93	3.864 ± 0.002	3.211 ± 0.015
	0.292 ± 0.003	1210	0.169 ± 0.003	0.6515	47.73	3.377 ± 0.004	2.854 ± 0.002
	0.471 ± 0.003	1311	0.167 ± 0.002	0.5385	50.34	3.031 ± 0.003	2.561 ± 0.003
	0.698 ± 0.000	1230	0.150 ± 0.001	0.4266	53.59	2.618 ± 0.001	2.262 ± 0.000
	0.896 ± 0.003	1030	0.144 ± 0.003	0.3334	56.22	2.194 ± 0.005	1.913 ± 0.001
	0.945 ± 0.002	1187	0.143 ± 0.002	0.3163	56.82	2.115 ± 0.004	1.849 ± 0.000
	1	---	---	0.2956[a]	57.47[a]	---	1.760[a]
573	0	---	---	1.0372	43.90	4.719	---
	0.048 ± 0.001	1206	0.158 ± 0.010	0.9863	44.60	4.593 ± 0.002	3.872 ± 0.043
	0.090 ± 0.003	1091	0.168 ± 0.009	0.9458	45.22	4.500 ± 0.004	3.754 ± 0.039
	0.295 ± 0.001	1299	0.158 ± 0.001	0.7563	48.28	3.961 ± 0.002	3.363 ± 0.005
	0.475 ± 0.004	1285	0.143 ± 0.002	0.6299	50.98	3.555 ± 0.004	3.078 ± 0.004
	0.682 ± 0.004	1140	0.132 ± 0.001	0.5154	54.03	3.147 ± 0.003	2.765 ± 0.002
	0.893 ± 0.004	1284	0.104 ± 0.005	0.4086	56.88	2.632 ± 0.001	2.382 ± 0.000
	0.944 ± 0.001	1189	0.109 ± 0.001	0.3880	57.51	2.551 ± 0.003	2.298 ± 0.000
	1	---	---	0.3674[a]	58.16[a]	---	2.214[a]
603	0	---	---	1.1620	44.26	5.330	---
	0.055 ± 0.001	1211	0.151 ± 0.007	1.1083	45.09	5.223 ± 0.002	4.437 ± 0.037
	0.089 ± 0.002	1130	0.150 ± 0.002	1.0547	45.61	5.052 ± 0.003	4.300 ± 0.032
	0.282 ± 0.005	1190	0.145 ± 0.004	0.8779	48.60	4.603 ± 0.006	3.961 ± 0.014
	0.475 ± 0.002	1287	0.141 ± 0.002	0.7237	51.60	4.129 ± 0.004	3.584 ± 0.004
	0.681 ± 0.004	1265	0.129 ± 0.002	0.5980	54.70	3.689 ± 0.005	3.250 ± 0.003
	0.881 ± 0.005	1278	0.124 ± 0.003	0.4930	57.44	3.256 ± 0.008	2.892 ± 0.002
	0.945 ± 0.000	1194	0.105 ± 0.001	0.4640	58.23	3.076 ± 0.003	2.784 ± 0.000
	1	---	---	0.4391	58.86	---	2.678
623	0	---	---	1.2452	44.50	5.742	---
	0.051 ± 0.002	1197	0.148 ± 0.010	1.1896	45.29	5.626 ± 0.003	4.794 ± 0.055
	0.096 ± 0.002	1195	0.137 ± 0.007	1.1340	45.99	5.476 ± 0.004	4.733 ± 0.037
	0.287 ± 0.001	1136	0.132 ± 0.002	0.9437	49.02	4.976 ± 0.003	4.341 ± 0.008
	0.480 ± 0.001	1295	0.127 ± 0.001	0.7826	52.09	4.483 ± 0.002	3.945 ± 0.002
	0.682 ± 0.004	1410	0.124 ± 0.002	0.6516	55.19	4.043 ± 0.007	3.579 ± 0.003
	0.890 ± 0.005	1367	0.112 ± 0.003	0.5391	58.04	3.568 ± 0.009	3.203 ± 0.002
	0.947 ± 0.003	1237	0.097 ± 0.004	0.5104	58.74	3.395 ± 0.011	3.091 ± 0.001
	1	---	---	0.4870	59.34	---	2.995

[a] The value below the melting point is the extrapolated one with respect to temperature.

Results

The relative difference in the internal cation mobilities is defined as

$$\varepsilon = (b_{Ag} - b_M)/(x_{Ag} b_{Ag} + x_M b_M), \tag{3}$$

where b_M is the internal mobility of cation M and x_M is the mole fraction of MNO_3. The obtained ε values are given in Tables 1 and 2 for the (Ag, Rb)NO_3 and (Ag, Cs)NO_3, respectively, together with the main experimental conditions.

The values of b_{Ag} and b_M are calculated from the ε values and the available data [3] on the densities and conductivities. The calculated internal mobilities are also given in Tables 1 and 2, and the corresponding isotherms at 543 K, 583 K, and 623 K are shown in Figs. 1 and 2, respectively.

Table 2. Relative differences in the internal mobilities in $(Ag, Cs)NO_3$ (the errors in ε are due to only the chemical analysis) and corresponding internal mobilities b_{Ag} and b_{Cs}

T/K	x_{Cs}	Q/C	ε	$\varkappa$ (10^2 S m^{-1})	V (10^{-6} m^3 mol^{-1})	b_{Ag} (10^{-8} m^2 V^{-1} s^{-1})	b_{Cs}
523	0	---	---	0.8293	43.18	3.711	---
	0.110 ± 0.001	852	0.215 ± 0.006	0.7210	45.69	3.495 ± 0.002	2.760 ± 0.020
	0.317 ± 0.002	834	0.248 ± 0.004	0.4946	50.32	2.783 ± 0.003	2.142 ± 0.007
	0.484 ± 0.001	846	0.215 ± 0.006	0.4000	53.93	2.493 ± 0.003	1.961 ± 0.003
543	0	---	---	0.9153	43.45	4.108	---
	0.109 ± 0.001	882	0.211 ± 0.005	0.7476	45.96	3.642 ± 0.002	2.890 ± 0.016
	0.287 ± 0.002	845	0.235 ± 0.003	0.5794	49.99	3.207 ± 0.003	2.499 ± 0.007
	0.514 ± 0.000	846	0.228 ± 0.002	0.4425	54.95	2.815 ± 0.003	2.241 ± 0.003
573	0	---	---	1.0452	43.85	4.750	---
	0.123 ± 0.001	802	0.201 ± 0.004	0.8895	46.73	4.414 ± 0.002	3.548 ± 0.018
	0.318 ± 0.001	806	0.219 ± 0.003	0.6499	51.21	3.691 ± 0.003	2.932 ± 0.007
	0.523 ± 0.003	802	0.203 ± 0.004	0.5043	55.75	3.224 ± 0.006	2.632 ± 0.005
603	0	---	---	1.1748	44.26	5.388	---
	0.109 ± 0.002	910	0.194 ± 0.007	1.0357	46.86	5.134 ± 0.004	4.155 ± 0.033
	0.305 ± 0.002	894	0.177 ± 0.002	0.7575	51.44	4.257 ± 0.003	3.540 ± 0.008
	0.513 ± 0.003	892	0.161 ± 0.002	0.5890	56.14	3.711 ± 0.005	3.158 ± 0.005
	0.691 ± 0.001	490	0.152 ± 0.003	0.5059	60.06	3.482 ± 0.008	3.001 ± 0.003
	1	---	---	0.3743[a]	66.93	---	2.596[a]
623	0	---	---	1.2612	44.54	5.821	---
	0.107 ± 0.001	818	0.193 ± 0.005	1.1144	47.12	5.555 ± 0.003	4.500 ± 0.027
	0.318 ± 0.003	823	0.165 ± 0.003	0.8062	52.10	4.583 ± 0.005	3.862 ± 0.010
	0.504 ± 0.007	827	0.157 ± 0.006	0.6508	56.26	4.097 ± 0.013	3.498 ± 0.013
	0.706 ± 0.005	423	0.119 ± 0.006	0.5441	60.85	3.745 ± 0.009	3.294 ± 0.004
	1	---	---	0.4122[a]	67.48[a]	---	2.882[a]

[a] See the footnote of Table 1. The values of $\varkappa$ and V for pure $AgNO_3$ are not exactly equal to those in Table 1 because the original data adopted in [3] are different.

Discussion

As seen from Fig. 1, the isotherms of both b_{Ag} and b_{Rb} decrease with increasing x_{Rb}, the decreasing rate being greater in the former than in the latter. This is a trend usually found and interpreted previously [8, 9].

Since the mobility of Ag^+ is quite similar to that of Na^+ in molten nitrates [2] and the molar volume of $AgNO_3$ is also similar to that of $NaNO_3$, the isotherms at 623 K of the $(Ag, Rb)NO_3$ are compared with those of $(Na, Rb)NO_3$ previously measured [10] in Figure 3. The mobilities in $(Ag, Rb)NO_3$ are somewhat greater than the corresponding ones in $(Na, Rb)NO_3$. This may be mainly because the molar volume of the former is somewhat smaller than the latter, whereas the ionic radius of Ag^+ is greater than that of Na^+ [2]; for example, at 623 K, $V(AgNO_3) = 44.49 \times 10^{-6}\ m^3\ mol^{-1}$ and $V(NaNO_3) = 44.95 \times 10^{-6}\ m^3\ mol^{-1}$. In the latter system b_{Na} decreases considerably in a rather anomalous way at very high concentration of x_{Rb}, which causes the Chemla effect. On the other hand, in the present system the Chemla effect does not occur in the investigated region ($x_{Rb} < 0.95$ and $T \leqq 623$ K). Since the difference in the ionic radii of Ag^+ and Rb^+ is somewhat smaller than that of Na^+ and Rb^+, it is reasonable that the Chemla crossing point is not observed in $(Ag, Rb)NO_3$ in the present experimental region, while it appears in $(Na, Rb)NO_3$ at very high x_{Rb}. In general, as the relative difference in the ionic radii of two cations is more different, the Chemla effect occurs more readily.

Since the melting point of $CsNO_3$ is relatively high (687 K), and the decomposition point of $AgNO_3$ is relatively low, the measurable region of temperatures and concentrations is limited, as reflected in Figure 2. The trend of the isotherms in $(Ag, Cs)NO_3$ is similar to that in $(Ag, Rb)NO_3$.

The isotherms at 623 K are compared with those in $(Na, Cs)NO_3$ [11] in Figure 4. The Chemla effect is observed in the latter but not in the former. This is presumably because the investigated region for $(Ag, Cs)NO_3$ is limited.

Figures 1 and 2 show that b_{Ag} is greater than b_{Rb} or b_{Cs} at all the investigated temperatures and composi-

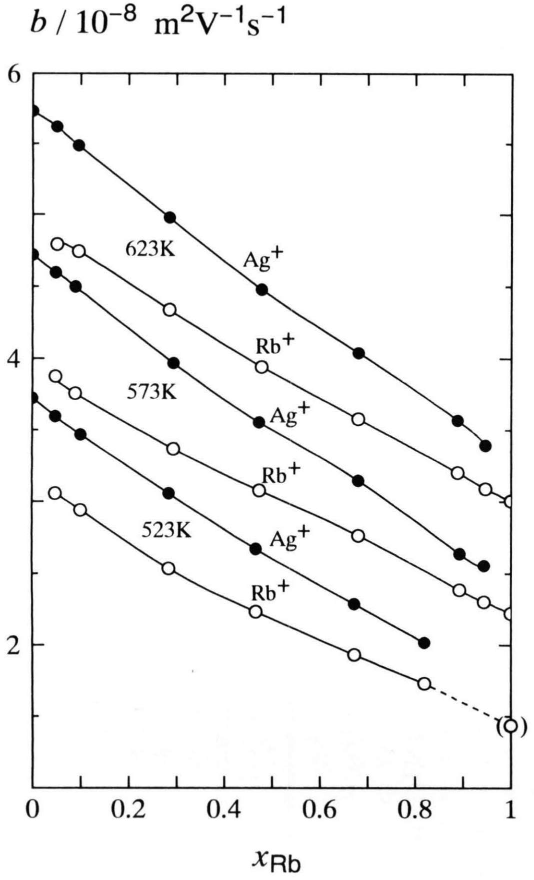

Fig. 1. Isotherms of b_{Ag} and b_{Rb} at 523 K, 573 K, and 623 K. The value in parentheses, being below the melting point, is extrapolated with respect to temperature.

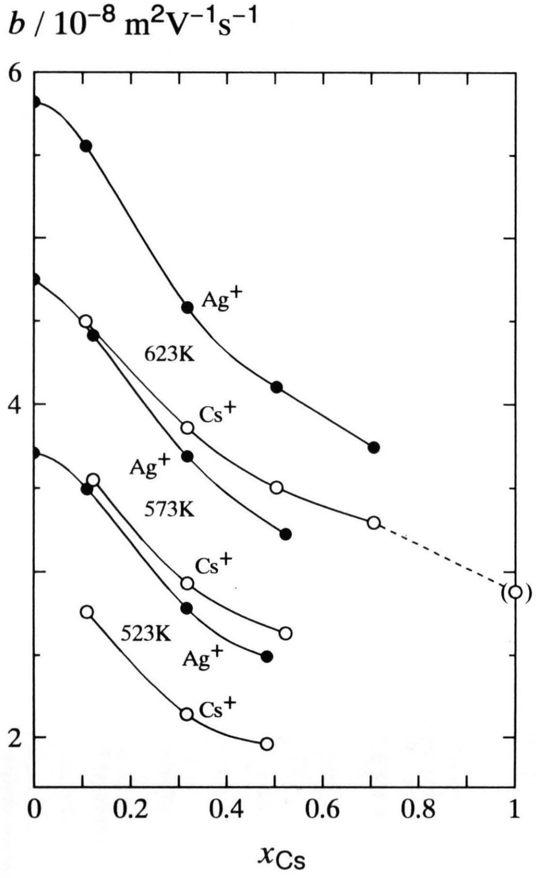

Fig. 2. Isotherms of b_{Ag} and b_{Cs} at 523 K, 573 K, and 623 K. As for the value in parentheses see Figure 1.

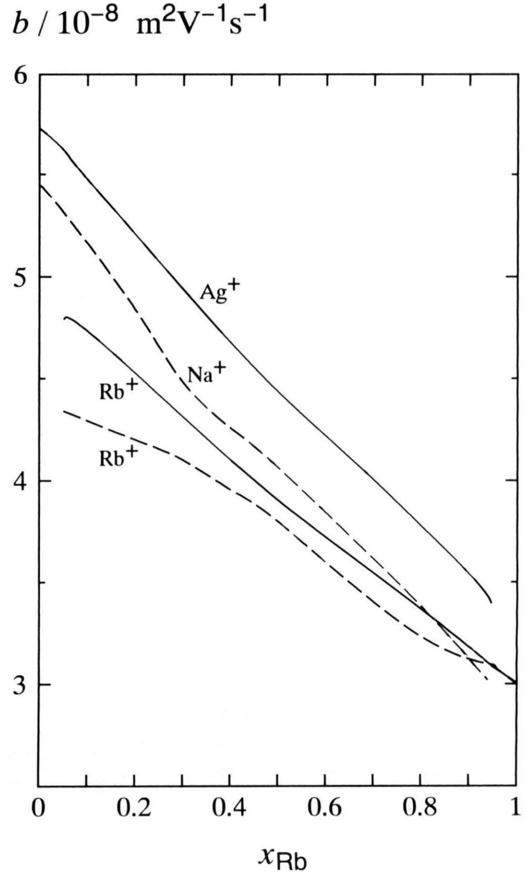

Fig. 3. Comparison of b_{Ag} in (Ag, Rb)NO_3 with b_{Na} in (Na, Rb)NO_3 [10] at 623 K. —: the former system, ---: the latter system.

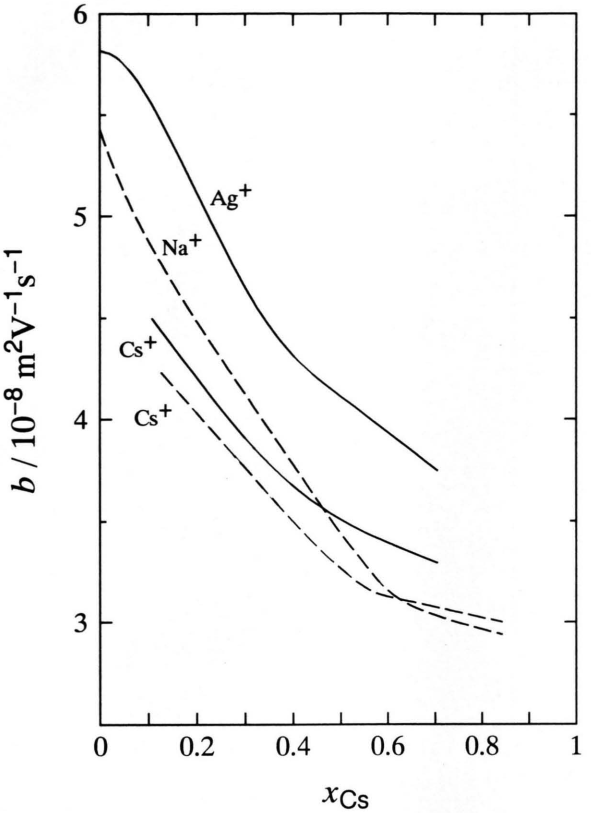

Fig. 4. Comparison of b_{Ag} in (Ag, Cs)NO_3 with b_{Na} in (Na, Cs)NO_3 [11] at 623 K. —: the former system, ---: the latter system.

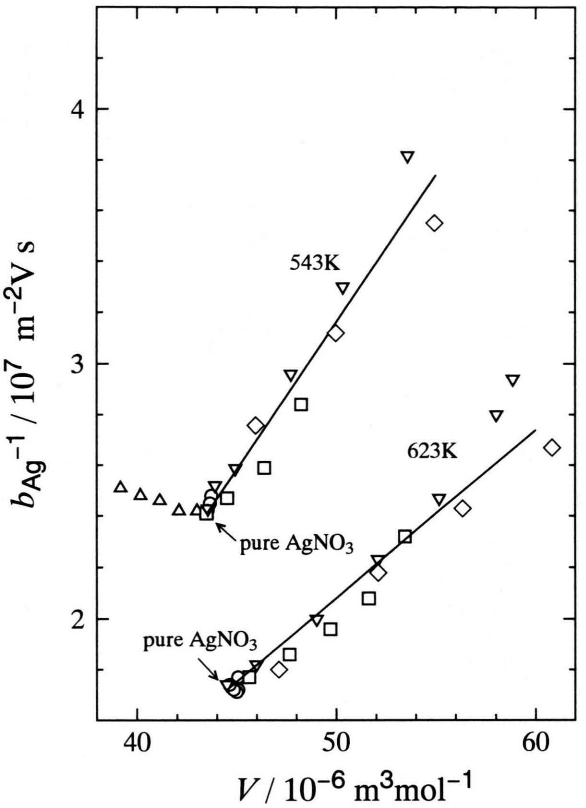

Fig. 5. b_{Ag}^{-1} vs. V in binary (Ag, M)NO_3. The solid lines are drawn according to (4) with the parameters in Table 3. △: M = Li [1], ○: Na [2], □: K [1], ▽: Rb, ◇: Cs.

tions. Thus, the mobilities of Ag^+ are greater than those of any other alkali ions in the binary systems (Ag, M)NO_3 (M = Li [1], Na [2], K [1], Rb and Cs) in all the investigated regions. However, if $AgNO_3$ could be heated to higher temperature without thermal decomposition, the Chemla effect would occur at high concentration of $CsNO_3$ in (Ag, Cs)NO_3, for example.

For the molten binary alkali nitrates, the internal mobilities particularly of small cations, that is, Li^+, Na^+ and K^+, are found to be expressed by [8, 11]

$$b = [A/(V - V_0)] \exp(-E/RT), \qquad (4)$$

where A and E are constants independent of co-cations and V_0 is a constant slightly dependent on temperature. In order to learn if such a relation holds also for b_{Ag} in binary mixtures (Ag, M)NO_3, the reciprocal values of b_{Ag} in the binary systems so far studied by the Klemm method are plotted against the molar volume V at 543 K and 623 K in Figure 5. Figure 5 reveals that (4) holds for b_{Ag}, though the b_{Ag} values seem to be more dependent on the co-cations than b_M in binary alkali nitrates do. The calculated parameters of (4) for b_{Ag} are given in Table 3 together with those for b_{Li}, b_{Na}, and b_K.

The general profile of b_{Ag}^{-1} vs. V shown in Fig. 5 resembles that of b_{Na}^{-1} [12]. At high x_{Rb} in the mixture with $RbNO_3$, b_{Ag}^{-1}, like b_{Na}^{-1}, deviates positively from the lines calculated for the other mixtures. In the mixture with $LiNO_3$, b_{Ag}^{-1} increases with decreasing molar V. In other words, b_{Ag} decreases with increasing concentration of Li^+ ions. This may be ascribed to the free space effect and/or the tranquillisation effect by Li^+ ions [8]. Since, with decreasing temperature, the decrease of b_{Ag} in (Ag, Li)NO_3 becomes more pronounced [1], this could be due to the free space effect rather than to the tranquillisation effect. Usually, the tranquillisation effect is more pronounced at higher temperatures.

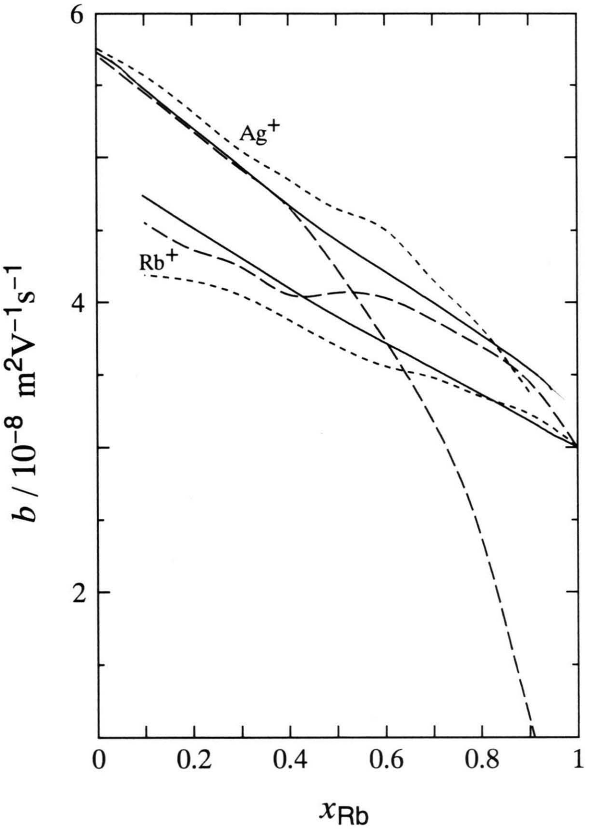

Fig. 6. Comparison of b_{Ag} and b_{Rb} in $(Ag, Rb)NO_3$ at 623 K determined in the present work with those previously determined by the EMF method. ····: EMF (A) [4], - - -: EMF (B) [5], —: this work.

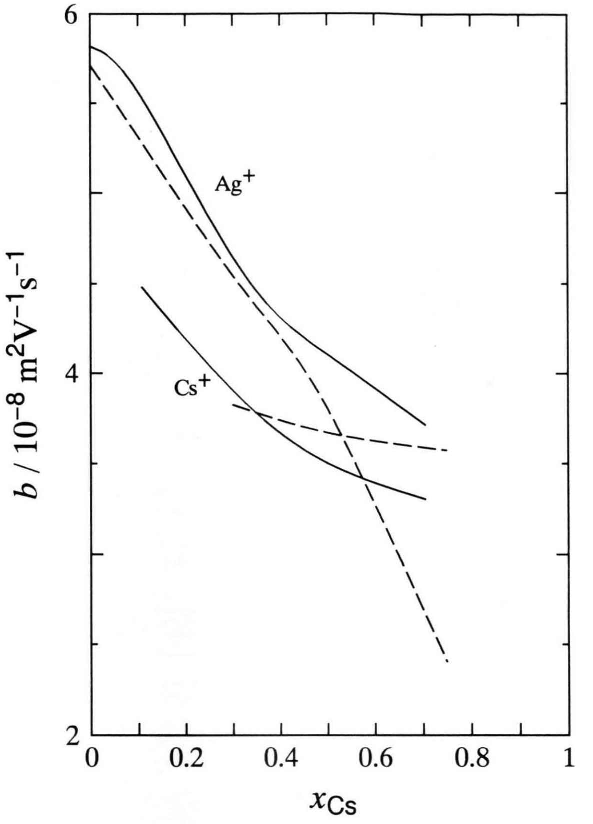

Fig. 7. Comparison of b_{Ag} and b_{Cs} in $(Ag, Cs)NO_3$ determined at 623 K in the present work with those previously determined by the EMF (B) method. - - -: [5], —: this work.

As stated in the Introduction, the internal mobilities in $(Ag, Rb)NO_3$ were measured at 523 K, 573 K and 623 K by the EMF (A) method [4] and at 623 K by the EMF (B) method [5]. The isotherms at 623 K are shown in Figure 6. A comparison with the present result reveals that the present data are in fair agreement with those of the EMF (A) method but in disagreement with those of the EMF (B) method in that no crossing occurs in the present results while a crossing point appears in the EMF (B) method. Possible reasons for this disagreement have been previously discussed [1, 2]. The Klemm method is superior to the EMF method in the accuracy of the internal transport number, particularly in the low concentration region of either cation.

The internal mobilities in $(Ag, Cs)NO_3$ were measured at 623 K only by the EMF (B) method [5]. As shown in Fig. 7, the present results do not agree with those of the EMF (B) method.

Table 3. Parameters of (4).

Cation	A (10^{-11} $m^5 V^{-1}$ $\cdot s^{-1}$ mol^{-1})	E (kJ mol^{-1})	V_0 (10^{-6} m^3 $\cdot mol^{-1}$)	Ref.
Li	2.84	17.80	24.7	[8]
Na	4.94	21.31	34.97−0.028 (T/K)	[8]
K	3.95	18.00	22.1	[8]
Ag	7.01	19.86	49.05−0.048 (T/K)	this work

Conclusion

Internal cation mobilities have been remeasured for the molten binary systems $(Ag, Rb)NO_3$ and $(Ag, Cs)NO_3$ by the Klemm method. More accurate and precise values than those measured by the EMF method can be obtained. The Chemla effect does not occur in these systems in the investigated regions. The internal mobilities of Ag^+, b_{Ag}, are compared also with b_{Ag} for other mixtures $(Ag, M)NO_3$ (M: Li, Na, and K); in all the investigated regions of temperatures and concentrations, the internal mobilities of Ag^+ ions are greater than those of all alkali ions. The internal mobilities of Ag^+ ions in these mixtures broadly agree with those of Na^+ ions in the corresponding mixtures, and are well expressed by Eq. (4) except those in the mixture $(Ag, Li)NO_3$. It is ascertained that the behaviour in mobility of Ag^+ ion in molten nitrates resembles that of Na^+ ion.

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