Internal Cation Mobilities in Molten (K, $Dy_{1/3}$) Cl

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Internal cation mobility ratios in the molten system KCl-$DyCl_3$ have been measured at 1093 K by Klemm's countercurrent electromigration method. From these, and data available on the conductivities and molar volumes of the mixtures, the internal mobilities b of both cations have been calculated. With increasing concentration of Dy, b_K decreases. The decrease of b_K is attributed to the tranquilization effect by Dy^{3+} ions which strongly interact with Cl^- ions. With increasing concentration of K^+, b_{Dy} decreases; this may be attributed to the stronger association of Dy^{3+} with Cl^- ions due to the enhanced charge asymmetry of the two cations neighboring to the Cl^- ions. It could not been clarified whether a species such as $[DyCl_6]^{3-}$ is also an electrically-conducting species in the K^+ rich range.

Key words: Klemm Method, Internal Mobilities, Molten $DyCl_3$, Tranquilization Effect.

Introduction

Recently the separation of nuclear fission products by means of countercurrent electromigration in molten salts has been investigated [1]. This induced us to study the internal mobilities in molten KCl-$DyCl_3$ mixtures, dysprosium being one of the main fission products. The internal mobilities of $(M_1, M_{2\,1/3})X$ are still unknown, whereas the conductivities of some such chloride systems can be found in the literature [2–5].

The countercurrent electromigration method (the Klemm method [6, 7]), with which we have previously measured the internal mobilities of $(M_1, M_{2\,1/2})X$ systems, such as KCl-$CaCl_2$ [8], was also applied in the present study.

Experimental

$DyCl_3$ was prepared by the reaction of Dy_2O_3 (Mitsui Mining Smelting Company, Ltd.) with an excess of NH_4Cl. The product was purified by sublimation at 1000 °C under reduced pressure to remove gases such NH_3 and HCl, residual NH_4Cl and impurities such as DyOCl. The details of the purification procedure are described in [9]. The electromigration cell was similar to that shown in Fig. 1 of [10]. With a temperature controller, the temperature was kept at (820 ± 2) °C. After electromigration for several hours, the separation tube was taken out of the large container and cut into several pieces for determining the K^+- and Dy^{3+}-content with emission spectrophotometry and ICP spectrometry, respectively.

The phase diagram of the present system is available [11]. The mixture of the composition K_3DyCl_6 has a congruent melting point at 805 °C, which is higher than those of pure KCl (775 °C) and pure $DyCl_3$ (655 °C). Therefore, the electromigration was performed at 820 °C, whereas we often performed electromigrations at 800 °C.

Results and Discussion

Since the difference in the mobilities of K^+ and Dy^{3+} is large, these ions were easily separated by electromigration. Therefore, not much electric charge could be transported without solidification of part of the melt, which, in turn, inevitably involved relatively large errors of ε; ε is defined by (A 5) in the Appendix.

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Table 1. Main experimental conditions and the internal mobilities in the molten system (K, Dy$_{1/3}$)Cl at 1093 K.

x_{Dy} [a] (y_{Dy}) [b]	Q (C)	ε [a]	$\varkappa$ [12] (S m^{-1})	V_m(V_e) [c] [12] (10^{-6} m^3 mol^{-1})	b_K [a]	b_{Dy} [a]
					(10^{-8} m^2 V^{-1} s^{-1})	
0			227	49.04	11.55	
0.096 ± 0.002 (0.241 ± 0.005)	1411	1.20 ± 0.02	174	52.87 (44.38)	10.28 ± 0.00	0.69 ± 0.12
0.194 ± 0.001 (0.420 ± 0.002)	610	1.56 ± 0.02	141	56.09 (40.38)	9.79 ± 0.05	0.54 ± 0.06
0.275 ± 0.028 (0.532 ± 0.035)	617	1.40 ± 0.06	123	58.98 (38.06)	8.45 ± 0.28	1.68 ± 0.27
0.404 ± 0.013 (0.670 ± 0.012)	536	2.10 ± 0.03	103	63.65 (35.22)	9.05 ± 0.13	1.15 ± 0.20
0.514 ± 0.003 (0.760 ± 0.002)	2089	1.38 ± 0.00	91.4	67.64 (33.37)	6.48 ± 0.01	2.11 ± 0.00
0.630 ± 0.000 (0.836 ± 0.000)	684	1.80 ± 0.01	82.8	71.84 (31.80)	6.84 ± 0.03	1.92 ± 0.01
0.778 ± 0.009 (0.913 ± 0.004)	649	1.95 ± 0.02	74.7	77.16 (30.20)	6.51 ± 0.05	1.94 ± 0.02
0.851 ± 0.005 (0.945 ± 0.002)	1184	1.58 ± 0.02	71.8	79.84 (29.55)	5.49 ± 0.04	2.01 ± 0.01
1			67.0	85.23 (28.41)		1.97

[a] The sign ± for x_{Dy}, y_{Dy}, ε and b indicates the errors due to the chemical analysis.
[b] The values in the parentheses are the equivalent fractions of Dy.
[c] The values in the parentheses are the equivalent volumes in 10^{-6} m^3 eq^{-1}.

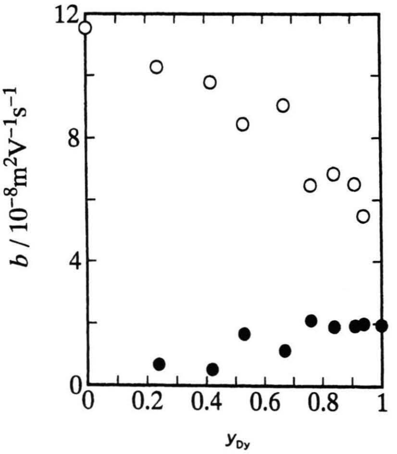

Fig. 1. Isotherms of b_K and b_{Dy} in the molten system KCl-Dy$_{(1/3)}$Cl at 1093 K. ○: b_K, ●: b_{Dy}.

The obtained ε values are given in Table 1 together with the main experimental conditions and the calculated internal mobilities.

The b values of K$^+$ and Dy^{3+} are calculated from the ε values and data available on the electrical conductivities $\varkappa$ [12] and equivalent volumes V_e [12] of the mixtures:

$$b_K = (\varkappa V_e/F)(1+\varepsilon y_{Dy}), \tag{1a}$$

$$b_{Dy} = (\varkappa V_e/F)(1-\varepsilon y_K), \tag{1b}$$

where y is the equivalent fraction. In the present paper, Dy$_{1/3}$Cl and DyCl$_3$ are regarded as the equivalent and molar units, respectively.

It should be mentioned that in the present case ε is not the relative difference in the internal mobilities, since b_c is not the average cation mobility [10, 13]. The average cation mobility b_{ac} may be expressed by

$$b_{ac} = x_K b_K + x_{Dy} b_{Dy}, \tag{2}$$

where x_K and x_{Dy} are the mole fraction of KCl and DyCl$_3$, respectively; x is related to y by (A 8) and (A 9). The isotherms of b_K and b_{Dy} at 820 °C are shown in Figure 1. As the internal cation mobilities are measured with respect to the Cl$^-$ ions, instead of x_{Dy} the equivalent fraction y_{Dy} is taken here as the abscissa.

Internal Mobility of K$^+$

The mobility b_K decreases with increasing concentration of Dy^{3+} and is much greater than b_{Dy}, as expected (Figure 1). This tendency is similar to that in molten (K, Ca$_{1/2}$)Cl [8, 14].

It has previously been found that in molten binary alkali nitrates, the internal mobilities b_1 of cation 1 are well expressed by the empirical equation [15]

$$b_1 = \{A/(V_e - V_0)\} \exp(-E/RT), \tag{3}$$

where A, E and V_0 are nearly independent of the kind of the coexisting cations. The b_K's in the present system are plotted in Fig. 2 against the equivalent volume, together with those in the systems (Na, K)Cl [16] and (K, Ca$_{1/2}$)Cl [8] at the same temperature. The broken line is drawn assuming that (3) holds for b_K in (Na, K)Cl. b_K in (Na, K)Cl increases with decreasing

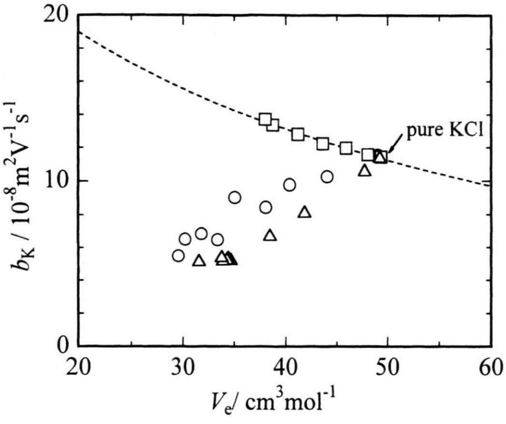

Fig. 2. Internal cation mobilities of K vs. equivalent volume in some molten binary systems. □: b_K in (Na, K)Cl [15], △: b_K in $(K, Ca_{1/2})Cl$ [8], ○: b_K in $Dy_{1/3})Cl$.

equivalent volume, as expected from (3). On the other hand, b_K in $(K, Ca_{1/2})Cl$ and $(K, Dy_{1/3})Cl$ decreases. In other words, b_K in $(K, Ca_{1/2})Cl$ and $(K, Dy_{1/3})Cl$ decreases with increasing concentration of Ca^{2+} and Dy^{3+}, respectively. This may be accounted for in terms of the tranquilization effect [13] by these cations on b_K. The tranquilization effect is assumed to occur by a strong coulombic interaction of (tranquilizer) cations with a common anion, that is Cl^- in the present case. Figure 2 shows that at a given equivalent volume the tranquilization effect of Ca^{2+} is stronger than that of Dy^{3+}, although the interaction of Ca^{2+}-Cl^- is probably weaker than that of Dy^{3+}-Cl^-. This apparent contradiction may be explained in terms of the difference in the number of these cations per Cl^- ion. The ratio of the numbers of Ca^{2+} per Cl^- is 1/2 and that of Dy^{3+} per Cl^- is 1/3, and thus the more effective tranquilization effect by Ca^{2+} than by Dy^{3+} is due to the greater number density of the divalent cation.

Internal Mobility of Dy^{3+}

The increase of b_{Dy} with increasing concentration of Dy^{3+} may be surprising because such an increase of the slower cation with its equivalent fraction does not occur in chloride systems with equal valency of its two cations. It does occur, however, if the slower cation has a higher valency than the faster cation. Examples may be the systems $(Na, Ca_{1/2})Cl$, $(K, Ca_{1/2})Cl$, $(Rb, Ca_{1/2})Cl$ [14] and $(Cs, Ca_{1/2})Cl$ [17], which were obtained by the EMF(A) method [18]; on the other hand, in $(Li, Ca_{1/2})Cl$, b_{Ca} shows opposite behavior [14]. The ratios of the equivalent volumes of the involved pure salts at 800 °C are $V_{Ca_{1/2}Cl}/V_{LiCl}=0.90$, $V_{Ca_{1/2}Cl}/V_{NaCl}=0.71$, $V_{Ca_{1/2}Cl}/V_{KCl}=0.54$, $V_{Ca_{1/2}Cl}/V_{RbCl}=0.48$ and $V_{Ca_{1/2}Cl}/V_{CsCl}=0.42$. Thus, the decrease of b_{Ca} with decreasing concentration of Ca^{2+}, with the exception of $(Li, Ca_{1/2})Cl$, could be accounted for by the increase in the equivalent volumes. However, our data on b_{Ca} in $(K, Ca_{1/2})Cl$ [8] obtained by the Klemm method do not necessarily agree with theirs [14]; In our data, b_{Ca} is nearly constant over the investigated concentration range. Thus, we will not further discuss b_{Ca} of these mixtures until these systems are remeasured by the Klemm method.

At any rate, one should consider the equivalent volume but not the molar volume of $DyCl_3$ or $CaCl_2$, because the average distance between the reference Cl^- ions, which corresponds to the equivalent volume, may be explicitly related to the cation internal mobilities through the self-exchange velocity [19].

We assume that the decrease of b_{Dy} with decreasing concentration of Dy^{3+} may be caused mainly by the charge-asymmetry stated below rather than by the increase in the equivalent volume. Owing to the charge asymmetry of the coordinating cations about the Cl^- ions, the Cl^- ions will more strongly associate to the Dy^{3+} ions and consequently associates such as $[DyCl_6]^{3-}$ will have a longer life time.

b_{Dy} measured in $(K, Dy_{1/3})Cl$ is plotted against the equivalent volume V_e in Fig. 3, where b_{Dy}'s in the sys-

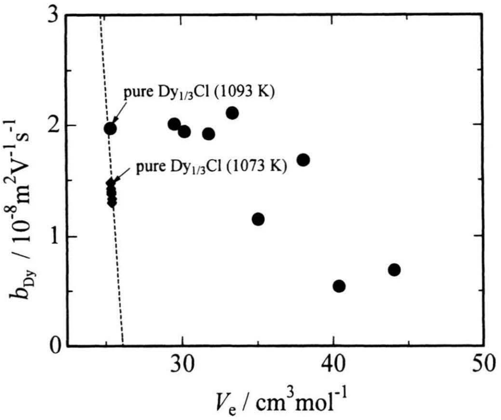

Fig. 3. Internal cation mobilities of Dy vs. equivalent volume in some molten binary systems. The equivalent volume of pure $Dy_{1/3}Cl$ appears to be slightly smaller at 1093 K [12] than at 1073 K [30]. This inconsistency comes from the different origins of the cited references. ●: b_{Dy} in $(K, Dy_{1/3})Cl$, ◆: b_{Dy} in $(Y, Dy_{1/3})Cl$ [29].

tem (Y, Dy)$_{1/3}$ Cl [20], previously measured at 1073 K, are also shown for comparison. Although b_{Dy} in the present system decreases with increasing equivalent volume, it decreases much less than in (Y, Dy)$_{1/3}$Cl. Raman spectroscopic studies suggest that there exist such species as $[LnCl_6]^{3-}$ in the mixture system (KCl-LnCl$_3$) (Ln: La [21, 22], Y [23], Gd [24]). Neutron and X-ray diffraction studies of pure LnCl$_3$ melts also suggest that even in the pure melts the octahedral unit exists, which is connected to other units by edge- or corner-sharing (LN: Y (neutron) [25], Nd (X-ray) [26], La, Ce, Pr, Nd, Gd, Dy and Sm (X-ray) [27]). X-ray diffraction has been performed also for a mixture melt of the composition K_3DyCl_6 [28].

Figure 1 suggests that at $y_K >$ ca. 0.5 ($y_K = 0.5$, i.e. $x_K = 0.75$, corresponds to K_3DyCl_6) b_{Dy} becomes particularly small. As stated above, this is presumably because the long-lived species $[LnCl_6]^{3-}$ is formed. This would not necessarily lead to the conclusion, however, that in this concentration range $[DyCl_6]^{3-}$ contributes to the internal mobility. This could be examined by studying the isotope effect of Dy in electromigration. We have not yet succeeded in measuring the electromigration isotope effect of Dy in mixtures rich in K^+ because in such mixtures K^+ and Dy^{3+} were separated before enough electric current for isotope effect measurements was passed. On the other hand, measurement of the isotope effect of Dy in pure molten DyCl$_3$ suggests that the electrically-conducting species containing Dy is Dy^{3+} [29].

The formation of such species as $[DyCl_6]^{3-}$ with increasing x_K could be explained based on the coulombic interaction. Figure 1 also shows that b_{Dy} seems to be nearly constant at least in the range $0 < y_K < 0.3$. This demonstrates that in this range the electrically-conducting species of Dy does not change much, and is therefore assumed to be mainly Dy^{3+}, although $[DyCl_6]^{3-}$ may be expected to exist partially.

Figure 3 shows that, as V_e increases, b_{Dy} in (K, Dy$_{1/3}$)Cl does not decrease so much as b_{Dy} in (Y, Dy)$_{1/3}$Cl [20]. With increasing equivalent volume, that is with increasing y_K, the number of more free Cl^- ions will increase. This in turn will make the separating motion of Dy^{3+} from Cl^- favourable to some extent, which is called the agitation effect of K^+ on b_{Dy}. In the system (K, Ca$_{1/2}$)Cl, with V_e, that is with increasing y_K, b_{Ca} does not vary much [8]. In both cases the two opposite effects mentioned above, that is the association and the agitation, are assumed to be superimposed on b_{Dy} and b_{Ca}. In the former case, however, the association may be more pronounced than in the latter case.

Conclusion

Internal cation mobilities in the molten binary system (K, Dy$_{1/3}$)Cl have been measured at 820 °C by Klemm's countercurrent electromigration. This was the first trial of this method appplied to a molten (monovalent + trivalent) cation mixture system with a common anion. b_K is much (ca. 3 – 10 times) greater than b_{Dy} in the whole concentration range, as expected. Thus, this method may be used for effective separation of rare earth ions from alkali ions.

As the concentration of Dy^{3+} increases, b_K considerably decreases. This decrease is ascribed to the tranquilization effect by Dy^{3+} which strongly interacts with common Cl^- ions.

As the concentration of K^+ increases, b_{Dy} gradually decreases and becomes very small at concentrations rich in KCl. This decrease may be attributed to a promoted association of species containing Dy^{3+} and generation of the long-lived species $[DyCl_6]^{3-}$. It could not be concluded by the present experiment, however, whether the electrically-conducting species containing Dy is cationic or anionic in the concentration range rich in KCl.

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Appendix

This Appendix aims at showing how from a countercurrent-electromigration experiment on a salt-mixture $(M_1, M_{2\,1/v})X$, where v is the valency of the second cation, the first being monovalent, one obtains the ratio b_1/b_2 of the internal mobilities of the cations, and from b_1/b_2, the conductivity $\varkappa$ and the molar volume V_m, one obtains b_1 and b_2.

In a countercurrent electromigration experiment on a system $(M_1, M_{2\,1/v})X$ the salt under study is filled into a tube containing a diaphragm for the suppression of convection. Direct current is passed through the tube, and the current-time integral $Q = F\,Z$ (F is the Faraday constant) is measured. After the electromigration one also measures the numbers of equivalents Z_1 and Z_2 existing in the melt situated between the anode and a cross-section A of the tube in a range where the original equivalent fractions y_1 and y_2 have not yet changed. From the values of Z, Z_1, Z_2, and y_1/y_2 the mobility-ratio b_1/b_2 can be determined.

In the region where grad y_1 and grad y_2 are still zero, for the transport-velocities holds

$$(v_i - v_3) = (v_i - v_A) - (v_3 - v_A), \quad (i=1,2). \quad \text{(A 1)}$$

Therefore, for the equivalent fluxes relative to 3 and A one has

$$J_{i3} = J_{iA} - y_i\, J_{3A}, \quad (i=1,2). \quad \text{(A 2)}$$

Integration over the time τ of the electromigration,

$$\int_0^\tau J_{i3}\,\mathrm{d}t = \int_0^\tau J_{iA}\,\mathrm{d}t - y_i \int_0^\tau J_{3A}\,\mathrm{d}t,$$

yields

$$k\, y_i\, b_i = \{Z_i - y_i(Z_1 + Z_2)\} - y_i\, Z, \; (i=1,2) \quad \text{(A 3)}$$

where k is a constant and $y_i(Z_1 + Z_2)$ is the number of equivalents of i which were between the anode and A before the electromigration. From (A 3) results

$$b_1/b_2 = \{Z - (y_2/y_1)\, Z_1 + Z_2\}/ \{Z - (y_1/y_2)\, Z_2 + Z_1\}. \quad \text{(A 4)}$$

Equation (A 4) can be easily transformed into the equation

$$\varepsilon \equiv (b_1 - b_2)/(y_1\, b_1 + y_2\, b_2) = (1/Z)\,\{(Z_2/y_2) - (Z_1/y_1)\} \quad \text{(A 5)}$$

used in [31].

The ratio b_1/b_2 can be expressed also in terms of ε by [12]

$$b_1/b_2 = (1 + \varepsilon\, y_2)/(1 - \varepsilon\, y_1). \quad \text{(A 6)}$$

Knowledge of the ratio b_1/b_2, the conductivity $\varkappa$ and the molar volume V_m allows for the determination of b_1 and b_2 by means of the equation

$$\varkappa = (x_1\, b_1 + x_2\, \nu\, b_2)\, F/V_m, \quad \text{(A 7)}$$

where x_1 and x_2 are mole fractions of the salts.

Equation (A 4) is identical with (64) in [18].

The following relations hold between mole fractions, x_1 and x_2, and equivalent fractions, y_1 and y_2:

$$x_1 = \nu\, y_1/[1 + (\nu - 1)\, y_1], \quad \text{(A 8 a)}$$

$$x_2 = y_2/[\nu + (1 - \nu)\, y_2]. \quad \text{(A 8 b)}$$

Therefore

$$y_1 = x_1/[\nu + (1 - \nu)\, x_1], \quad \text{(A 9 a)}$$

$$y_2 = \nu\, x_2/[1 + (\nu - 1)\, x_2]. \quad \text{(A 9 b)}$$

The equivalent volume V_e is related to the molar volume V_m by

$$V_e = (y_1/x_1)\, V_m = [1 + (1/\nu - 1)\, y_2]\, V_m. \quad \text{(A 10)}$$

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