New Empirical Formulae for the Mass Effect in the Countercurrent Electromigration of Molten Metal Halides

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The mass effect of the cation in the countercurrent migration of molten metal halides has long been known to correlate with the cation-to-anion mass ratio according to Klemm's formulae:[1,2]

$$\mu = -0.15/(1+m_+/2.1m_-)$$
(for halides with layer lattices)

and $$\mu = -0.078/(1+m_+/2.1m_-)$$
(for halides with coordination lattices)

where μ, m_+, and m_- stand for the mass effect, the mass of the cation, and the mass of the anion, respectively.

However, recent investigations[3-6] have revealed that there are several cases in which the values of μ calculated by the Klemm formulae deviate considerably from the experimental values. Although a new empirical formula for the same sort of correlation was proposed by Jordan and Klemm[5] in 1966, it applies only to a group of alkali halides.

After a careful examination of the available data on μ, we have found that a clear correlation exists between the mass effect and the cation-to-anion radius ratio of the halide. In Fig. 1, the experimental values of μ for various metal halides are plotted as a function of the cation-to-anion radius ratio.

We may see from Fig. 1 that a linear correlation exists between the mass effect and the cation-to-anion radius ratio of the halide. In addition, it is clear that the data for a group of monovalent metal halides show a linear correlation similar to, but clearly displaced from, the correlation line for a group of divalent metal halides.

Fitting the set of the data for each group of the halides in Fig. 1 to an equation of a linear form, $\mu=a(r_+/r_-)+b$, where a and b are constants, by a standard least-square procedure, we have obtained two empirical formulae:

$$\mu = 0.181(r_+/r_-) - 0.203$$
(for monovalent metal halides)

$$\mu = 0.233(r_+/r_-) - 0.185$$
(for divalent metal halides)

The experimental μ values of several halides are listed in Table 1, along with the values calculated by both Klemm's and our formulae.

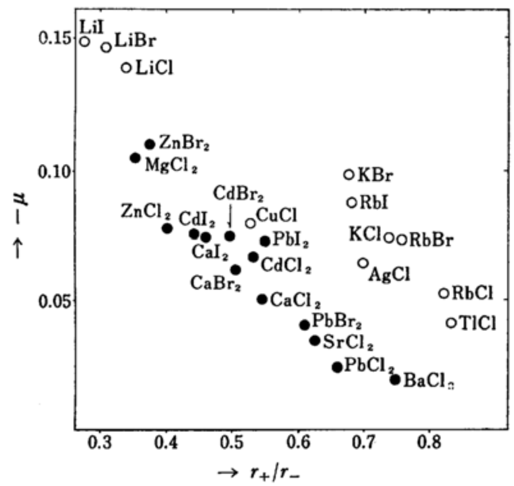

Fig. 1. Correlation of the mass effect of molten halides with the cation-to-anion radius ratio.
○ monovalent metal halide
● divalent metal halide
Sources of data: KBr and RbI—N. Saito, H. Kanno and I. Tomita, unpublished work; CaI_2, CdI_2 and PbI_2—J. Romanos and A. Klemm, *Z. Naturforsch.*, **19a**, 1000 (1964); $CdBr_2$—I. Holmlid, *ibid.*, **21a**, 270 (1966); other data—A. Klemm, "Molten Salt Chemistry," ed. by M. Blander, Interscience Publishers, New York, N. Y. (1964), p. 597.

TABLE 1. COMPARISON OF THE CALCULATED μ VALUES WITH EXPERIMENTAL DATA

Salt	$-\mu$ Found by experiments	$-\mu$ Calculated by Saito-Kanno's formulae	$-\mu$ Calculated by Klemm's formulae
RbCl	0.052	0.054	0.070
RbBr	0.073	0.065	0.099
RbI	0.087	0.079	0.113
LiCl	0.140	0.142	0.138
AgCl	0.064	0.077	0.061
$CaCl_2$	0.051	0.058	0.050
$CaBr_2$	0.062	0.067	0.060
CaI_2	0.075	0.079	0.130

Detailed discussions of our formulae will appear in a full paper to be published elsewhere.

1) A. Klemm, *Z. Naturforsch.*, **6a**, 487 (1951); *ibid.*, **8a**, 397 (1953).
2) A. Neubert and A. Klemm, *ibid.*, **16a**, 685 (1961).
3) J. Romanos and A. Klemm, *ibid.*, **19a**, 1000 (1964).
4) I. Holmlid, *ibid.*, **21a**, 270 (1966).
5) S. Jordan and A. Klemm, *ibid.*, **21a**, 1581 (1966).
6) N. Saito, H. Kanno and I. Tomita, unpublished work.