Effective transport number in mixed electrolyte solutions

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Effective transport numbers of cations, in solution in which another cation having the same valency is added, have been calculated and experimentally determined by measuring EMF across the concentration cell. It has been found that values of calculated and experimentally determined effective transport number are in good agreement.

A few investigators have studied the transport number and activity coefficient in mixed salt solutions. Most of the investigators have given preference to the characteristics of membrane. The results reported by the various investigators are not in agreement and are contradictory in nature. We report here effective transport numbers in mixed electrolyte solutions determined by measuring EMF across the concentration cell.

Experimental measurement of EMF was done in the same way as described earlier.

When an electrolyte M'Clx is added in the left hand half cell of the cell,

\[ \text{Ag} / \text{AgCl} / MClx (a_1) / MClx (a_3) / \text{AgCl} / \text{Ag} \]  

the effective transport number of cation M'^x may be given empirically, as the sum of products of activity fractions of the electrolyte and the transport number of respective cations. Thus the effective transport number may be given as follows:

\[ t_{M'^x} = \frac{a_1 t_{M'^x} + a_3 t_{M'^x}}{a_1 + a_2} \]  

where \( a_1, a_2 \) and \( a_3 \) are mean activities of electrolytes in the solutions, \( x \) is the valence of \( M \) or \( M' \), \( t_{M'^x} \) and \( t_{M'^x} \) are transport numbers of cations \( M'^x \) and \( M'^{-x} \) respectively in free solutions.

Nerst equation can be modified as

\[ E_t = \frac{-RT \nu}{F} \ln \frac{a_1 + a_2}{a_3} \]

where \( \nu \) and \( x \) are the total number of ions and anions given by the one molecule of the electrolyte respectively.

The transport number of K' in the cell Ag / AgCl 0.10N KCl / 0.01N KCl AgCl / Ag as reported in the literature is 0.492 at 35°C. Effective transport number of K' as calculated by the Eq. (2) when 0.02N, 0.04N, 0.06N and 0.10N NaCl is added in the left side of the cell, has been found to be 0.485, 0.470, 0.462 and...
0.450 respectively. The corresponding effective transport number determined by the Eq. (3) has been found to be 0.479, 0.478, 0.469 and 0.452 respectively.

Similarly the transport number of Na⁺ in the cell Ag/AgCl 0.10N NaCl/0.01N NaCl AgCl/Ag as reported in the literature is 0.403 at 35°C. Effective transport number as calculated by the Eq. (2) when 0.02N, 0.04N, 0.06N and 0.10N KCl is added in the left side of the cell, has been found to be 0.419, 0.430, 0.441 and 0.450 respectively. The corresponding effective transport numbers as determined by the Eq. (3) are 0.417, 0.431, 0.438 and 0.442.

The above results show that when cations of lower transport number are added to the solution containing cations of higher transport number, the te⁺ of previously present cations decreases (Fig. 1) and when cations of higher transport number are added to the solution containing cations of lower transport number, the te⁺ of previously present cations increases (Fig. 2). These results also show that the calculated values of te⁺ by Eq. (2) are in good agreement with the values obtained by Eq. (3).

References