

Supporting Information

Extraction efficiency of mixed carrier systems

Extraction efficiency for the case that both the anion carrier and the cation carrier form a 1:1 complex with the anion and cation, respectively.

The extraction efficiency E for cooperative extraction of a salt MX by a mixture of an anion carrier and cation carrier as defined by eq A.1, can be calculated from:

(i) the partition constant K_p :

$$E = \frac{[M^+]_m + [ML_M^+]_m}{[L_X]_{0,m} + [L_M]_{0,m}} \times 100\% \quad (\text{A.1})$$

$$K_p = \frac{[M^+]_m [X^-]_m}{a_s^2} \quad (\text{A.1.1})$$

(ii) the complexation constants of the anion X^- ($K_{a,X}$) and cation M^+ ($K_{a,M}$) by the corresponding carrier (L_X denotes the anion carrier and L_M denotes the cation carrier):

$$K_{a,X} = \frac{[L_X X^-]_m}{[L_X]_m [X^-]_m} \quad (\text{A.1.2})$$

$$K_{a,M} = \frac{[L_M M^+]_m}{[L_M]_m [M^+]_m} \quad (\text{A.1.3})$$

(iii) the mass balances for the carriers L_X and L_M in the membrane phase:

$$[L_M]_{0,m} = [L_M]_m + [L_M M^+]_m \quad (\text{A.1.4})$$

$$[L_X]_{0,m} = [L_X]_m + [L_X X^-]_m \quad (\text{A.1.5})$$

(iv) the electroneutrality assumption:

$$[M^+]_m + [L_M M^+]_m = [X^-]_m + [L_X X^-]_m \quad (\text{A.1.6})$$

In order to simulate E , eqs A.1.1. - A.1.6 were rearranged to give eqs A.1.7 and A.1.9 (salt activities a_{aq} are used instead of salts concentrations $[M^+]_{aq}$ or $[X^-]_{aq}$).

$$[L_X]_{0,m} - \left(1 + \frac{K_{a,X} K_p a_{aq}^2}{[M^+]_m} \right) [L_X]_m = 0 \quad (A.1.7)$$

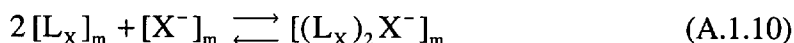
$$[L_M]_{0,m} - (1 + K_{a,M} [M^+]_m) [L_M]_m = 0 \quad (A.1.8)$$

$$[M^+]_m (K_{a,M} [L_M]_m + 1) - \frac{K_p a_{aq}^2}{[M^+]_m} (1 + K_{a,X} [L_X]_m) = 0 \quad (A.1.9)$$

The defined variables are: $K_{a,M}$, $K_{a,X}$, K_p , a_{aq} , $[L_X]_{0,m}$, $[L_M]_{0,m}$ and the unknowns are: $[M^+]_m$, $[L_X]_m$, $[L_M]_m$. The set of equations can be solved iteratively. Guess values for the unknowns are estimated to initialize the iteration process.³⁷ From the optimal values for $[M^+]_m$, $[L_X]_m$, $[L_M]_m$ and eqs A.1.1 - A.1.6, the extraction efficiency E (eq 8) was calculated.

Extraction efficiency for the case that the cation carrier forms a 1:1 complex and the anion carrier forms a 2:1 carrier/anion complex.

The partitioning of salt (K_p) is defined according to eq A.1.1 and the formation of a 1:1 cation:carrier complex is defined according to eq A.1.3. For the complexation of the anion X^- by the anion carrier L_X as a 2 : 1 complex:



we obtain

$$K_{a,X} = \frac{[(L_X)_2 X^-]_m}{[L_X]_m^2 [X^-]_m} \quad (A.1.11)$$

The mass balances for the cation carrier is defined by eq A.1.4 and the anion carrier is given by:

$$[L_X]_{0,m} = [L_X]_m + 2[(L_X)_2 X^-]_m \quad (A.1.12)$$

The electroneutrality constraint now becomes:

$$[M^+]_m + [L_M M^+]_m = [X^-]_m + [(L_X)_2 X^-]_m \quad (A.1.13)$$

The above set of eqs can be rearranged to give a set of 3 eqs; A.1.14 - A.1.16.

$$[L_X]_{0,m} - \left(1 + \frac{2K_{a,X} K_p a_{aq}^2 [L_X]_m}{[M^+]_m} \right) [L_X]_m = 0 \quad (A.1.14)$$

$$[L_M]_{0,m} - (1 + K_{a,M} [M^+]_m) [L_M]_m = 0 \quad (A.1.15)$$

$$[M^+]_m (1 + K_{a,M} [L_M]_m) - \frac{K_p a_{aq}^2}{[M^+]_m} (1 + K_{a,X} [L_X]_m^2) = 0 \quad (A.1.16)$$

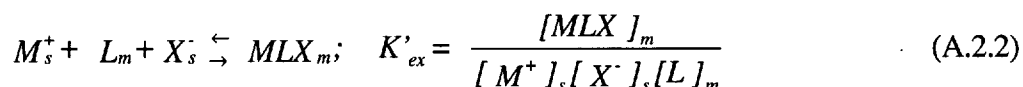
The defined variables are $K_{a,M}$, $K_{a,X}$, K_p , a_{aq} , $[L_X]_{0,m}$, $[L_M]_{0,m}$ and the unknown variables are $[M^+]_m$, $[L_X]_m$, $[L_M]_m$. The corresponding extraction efficiency E (eq 8) was calculated from the data obtained from the iteration process.³⁷

Transport model for facilitated transport of salt by a bifunctional receptor

In the case of initial transport under steady-state conditions, the corresponding flux is related to the complex concentration $[MLX]_{ms}$ at the source phase interface by equation A.2.1.

$$J_0 = \frac{D_m}{d_m} [MLX]_{ms} \quad (A.2.1)$$

For the calculation of the $[MLX]_{ms}$, it is assumed that the ditopic salt complex is primarily present in the membrane phase; $[XLM]_m \gg [XL^-]_m$ and $[XLM]_m \gg [LM^+]_m$. Furthermore, it is assumed that the complexation of the ion M^+ or X^- is not affected by the presence of the counter-ion in the complex. The binding constants for anion complexation $K_{a,X}$ by the carrier L and the by cation complex ML^+ are equal. The same holds for the complexation of the cation constant defined by $K_{a,M}$. The extraction of salt by bifunctional carrier L is then be defined according to equation A.2.2.



The extraction constant K_{ex}' is the product of the stability constant for anion complexation, cation complexation, and salt partitioning; $K_{ex}' = K_{a,M} K_{a,X} K_p$. When it is assumed that the total amount of carrier at the interface is constant (eq A.2.3), an expression for the initial flux J_0 by a bifunctional complex MLX is derived (eq A.2.4):

$$[L]_{0,ms} = [MLX]_{ms} + [L]_{ms} \quad (A.2.3)$$

$$J_0 = \frac{D_m K'_{ex} L_0}{d_m} \left[\frac{a_s^2}{(1 + K'_{ex} a_s^2)} \right] \quad (A.2.4)$$

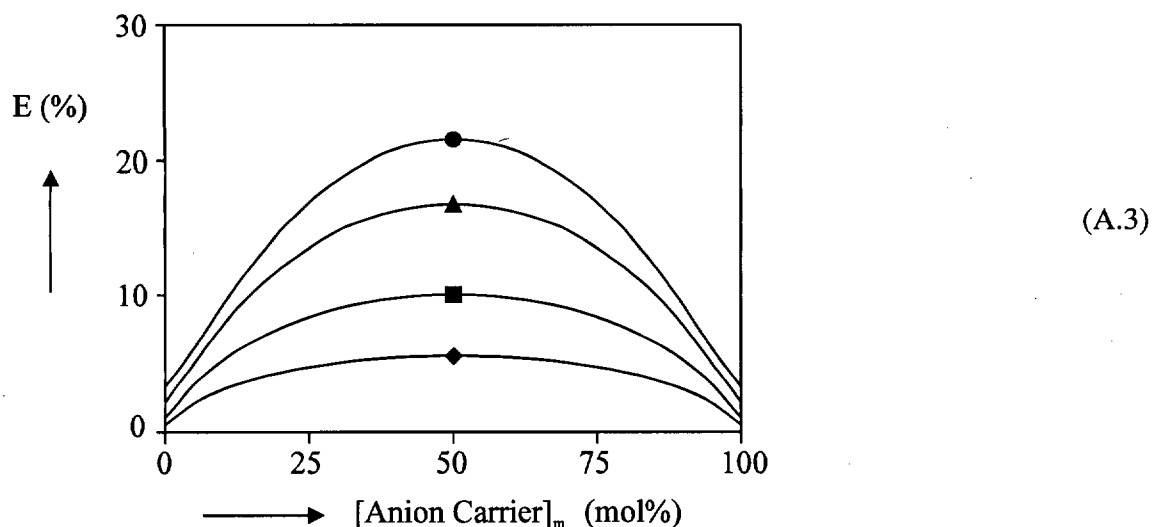


Figure A.3 Calculated extraction efficiency E for carrier mixtures as a function of the salt concentration a_{aq} ($K_p = 1 \times 10^{-10}$, $K_{a,M} = K_{a,X} = 5 \times 10^4 \text{ M}^{-1}$); $([L_X]_{0,m} + [L_M]_{0,m}) = 0.01 \text{ M}$, $a_{\text{aq}} = 0.25$ (\diamond), 0.5 (\blacksquare), 1.0 (\blacktriangle), and 1.5 (\bullet) M .

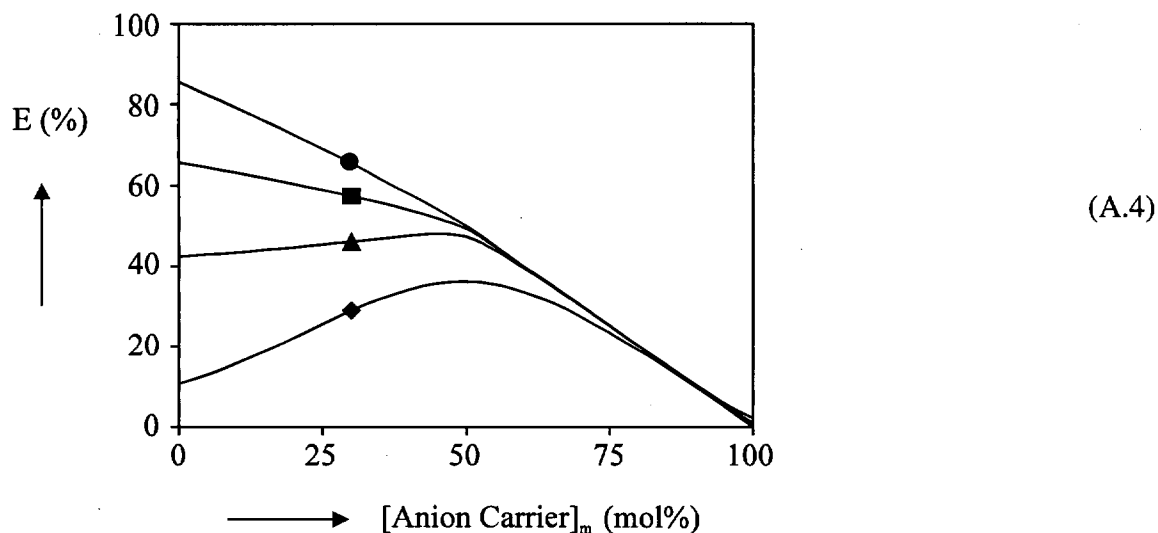


Figure A.4 Calculated extraction efficiency E for carrier mixtures as a function of the salt concentration a_{aq} ($K_p = 1 \times 10^{-10}$, $K_{a,M} = 5 \times 10^8 \text{ M}^{-1}$, $K_{a,X} = 5 \times 10^4 \text{ M}^{-1}$); $[L_M]_{0,m} + [L_X]_{0,m} = 0.01 \text{ M}$, $a_{\text{aq}} = 0.05$ (\diamond), 0.25 (\blacktriangle), 0.5 (\blacksquare), and 1.0 (\bullet) M .