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Standard formal potentials; Individual distribution constants; Extraction into nitrobenzene; Ion-pair formation constants; Potentiometry; 18-Crown-6 ether

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± 0.5 mol^{1} dm^{3} with b_s = (5.1 ± 0.5) × 10^{4} mol dm^{3} at R

The log K_{ex} and log $K_{ex\pm}$ values were in the orders A = F_3CCO_2 < ReO_4 < Dnp < MnO_4 < Pic. The log $K_{D,NaL}$ values were in the same order as those for log K_{ex} and log $K_{ex\pm}$. Also, the log $K_{D,A}$ values were in the order F_3CCO_2 ReO_4 < Pic < MnO_4 < Dnp.

The order of the log $K_{1,NB}$ values was F_3CCO_2 Dnp MnO_4 < ReO_4 < Pic. Ionic radii [21] of A are assumed to be H_3CCO_2 (2.32 Å) F_3CCO_2 < MnO_4 (2.40) < ReO_4 (2.60) < Dnp < Pic. On the other hand, the ion size parameters [16,22] in aqueous solutions were in the order MnO_4 (3.5) < ReO_4 (3.9) < H_3CCO_2 and H_2ClCCO_2 (4.5 Å) F_3CCO_2 < Dnp < Pic (7). Here, the positions for F_3CCO_2, Dnp and Pic

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K , K ,

The log $K_{D,NaLA}$ {= log ([NaLA]$_{NB}$/[NaLA])} value was calculated from the thermodynamic relation [15,17].

$$\log K_{D,NaLA} = \log K_{ex} \quad \log (K_{NaL} \tilde{} K_1) + \log K_{D,L}; \qquad (7)$$

since NaLA is a neutral ion pair, its distribution constant naturally satisfies the condition of $_{eq}$ = 0 V [26]. Here, the symbol K_1 is defined as [NaLA]/[NaL$^+$][A] (see Appendix A) and its values slightly changed with changes of I. The log $K_{D,NaLA}$ values obtained were 1.01 for A = MnO_4^-, 0.44 for ReO_4^-, 0.97 for $F_3CCO_2^-$ and 0.96 for Dnp, its value for Pic was reported to be 3.68 [11]. Figure 6 shows a plot of log $K_{D,NaLA}$ versus log $K_{D,A}^S$

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holds in the present extraction systems: log $K_{D,NaLA}$ = log $K_{D,A}^{S}$ + log ($K_{NaL,NB}$/K_{NaL}) + log ($K_{D,Na}^{S}$ ˜ $K_{D,18C6}$) + log ($K_{1,NB}$/K_{1}) log $K_{D,A}^{S}$ + 0.7_{2} + log ($K_{1,NB}$/K_{1}), although the coefficient of log $K_{D,A}^{S}$ was somewhat larger than unity. Here, this relation is derived from log K_{ex} = log $K_{ex\pm}$ + log $K_{1,NB}$ {see Equations (6) and (7)}. The average values of K_{1}/mol^{1} dm^{3} were $10^{1.77}$ for A = Pic, $10^{2.31}$ for MnO_4 , $10^{2.43}$ for ReO_4 , $10^{1.86}$ for Dnp and $10^{2.51}$ for F_3CCO_2 . Therefore, an estimate of the intercept, 0.7_{2} + log ($K_{1,NB}$/K_{1}), becomes in the range of 2.1 to 4.7. Its experimental value was 3.3_{2} ± 0.2_{3} (see the caption in Figure 6), overlapping this estimate. On the other hand, a plot of log $K_{D,NaLA}$ versus log $K_{D,A}$ at $_{eq}$ 0 V did not yield the correlation (R^2 = 0.038).

The authors clarified the presence of $_{eq}$ at the NB/w interfaces in the NaA extraction systems with 18C6, as well as the NaPic extraction one. Also, the positive correlation of log $K_{ex\pm}$ to $_{eq}$ among A was observed in a given combination of Na^{+}, NB, and 18C6. This fact makes the previously-reported correlation among L in given combinations of NaPic and diluents more-sure. Moreover, it was demonstrated that this method makes the $_{A}^{0\prime}$- or $K_{D,A}^{S}$-determination of a single A having the lower extraction-ability easier. In particular, using the more general L, such as 18C6, is important for the present method, because this promises the high versatility of the method.

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