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Mutual effects of oxo anions in extraction with tetraoctylammonium salts in polar solvents

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Mutual effects of perrhenate, permanganate, pertechnetate and perchlorate ions in extraction with quaternary ammonium salts in polar solvents has been studied.

Previously, we studied the extraction of MnO_4^-, TcO_4^-, RuO_4^-, and RuO_4^{2-} ions from neutral and weakly alkaline solutions with tetraoctylammonium salts in benzene and toluene. The concentration exchange constants of oxo anions for chloride and nitrate ions were estimated.[1,2] With the use of the exchange constants of chloride ions for bromide and hydroxide ions and published data,[3–6] it is possible to form a selectivity series for singly and doubly charged anions. For example, this series for singly charged anions is as follows:

$$MnO_4^- > RuO_4^- > TcO_4^- > ReO_4^- \geq ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > F^- > OH^-.$$

The exchange reaction during the extraction of singly charged oxo anions can be written as follows:

$$R_4NA_{(o)} + X^-_{(a)} = R_4NX_{(o)} + A^-_{(a)}, \qquad (1)$$

where $R_4NA_{(o)}$ is a tetraoctylammonium salt, A^- is the salt ion (in our case, it is the Br^- ion), X^- is the extracted oxo anion, and the subscripts (o) and (a) designate organic and aqueous phases, respectively.

In the absence of other reactions in organic and aqueous phases, we processed experimental results using the equation

$$\log D_X^- = \log K_{ex} + \log \frac{[R_4NA]_{(o)}}{[A^-]_{(a)}} \qquad (2)$$

where D_X^- is the distribution ratio of the oxo anion, K_{ex} is the exchange constant, and the expressions in brackets designate the equilibrium concentrations of substances.

The exchange constant is

$$K_{ex} = D_X^- / D_A^-. \qquad (3)$$

The slope of the linear plot of $\log D_X^-$ *vs.* $\log D_A^-$ corresponded to the charge of the oxo anion.

We used benzene and polar solvents (nitrobenzene, and its mixture with benzene in a volume ratio of 7:3) as diluents for quaternary ammonium (QA) salts.

We radiometrically determined the distribution ratios of rhenium using a scintillation detector with a NaI (Tl) crystal. Rhenium-188 was obtained from a $^{188}W(^{188}Re)$ generator. Tetraoctylammonium bromide was synthesised according to a published procedure.[2] The solvents were rectified;[7] NH_4ReO_4, $KMnO_4$, $KClO_4$ salts of analytical grade were used.

When studying the extraction of ammonium perrhenate with tetraoctylammonium bromide in nitrobenzene, we observed an increase in the distribution ratios of anions as compared with the benzene systems. At the same time, the concentration dependence of perrhenate distribution ratios took place (Figure 1). This phenomenon is difficult to explain because we found the concentration dependence of oxo anion distribution ratios even in benzene as a result of the competition of oxo anions with the QA counter ion during extraction exchange [equations (2), (3)].

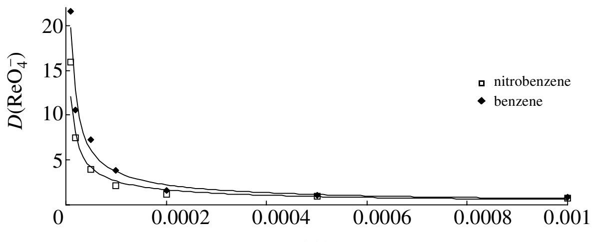

Figure 1 Back extraction of tetraoctylammonium perrhenate from nitrobenzene or benzene ($[R_4NReO_4]^{initial}_{(o)} = 10^{-3}$ mol dm^{-3}) by ammonium perrhenate solutions.

However, whereas in the benzene systems the slope of the linear plot of $\log D_X^-$ *vs.* $\log D_A^-$ corresponds to the oxo anion charge, for polar solvents such as diluents for QA salts the slope of this function does not correspond to the oxo anion charge. A reason for this difference could be partial dissociation of ion pairs in polar organic solvents.

To confirm this suggestion, we measured the electric conductivities of R_4NBr, R_4NClO_4, R_4NReO_4, R_4NTcO_4 and R_4NMnO_4 in nitrobenzene and calculated the dissociation constants of these salts.[8,9] We obtained the values 3.8×10^{-4}, 4.0×10^{-3}, 5.7×10^{-3}, 2.0×10^{-3} and 3.0×10^{-3} mol dm^{-3}, respectively ($\delta_{P=0.95} = 5$–8%).

Based on our studies, we made a supposition on a mutual effect of the oxo anions on extraction. This effect should be observed due to both the dissociation of extracted compounds in the organic phase and the presence of a QA cation as the common ion. However, this process depends on many factors and is more complicated for the quantitative description than the recently studied extraction of metal-halide acids by oxygen-containing solvents and metal cations by macrocyclic compounds.[10,11] Indeed, both the extracting agent and the ion pairs of extracted oxo anions dissociate in the organic phase, and the dissociation constants of all the salts are of the same order of magnitude. At the same time, the exchange constants of oxo anions for bromide ions (or other ions) differ considerably from one another, and their changes conform to the selectivity series but do not follow the changes in the dissociation constants. A change in the concentration of any component in the test system results in a change in the concentrations of other components.

Therefore, to simplify the system, we eliminated bromide ions using tetraoctylammonium perrhenate (10^{-3} mol dm^{-3}) as an extracting agent. Thus, the back extraction of perrhenate into the aqueous phase containing two oxo anions, *i.e.*, perrhenate and perchlorate (pertechnetate or permanganate), was investigated.

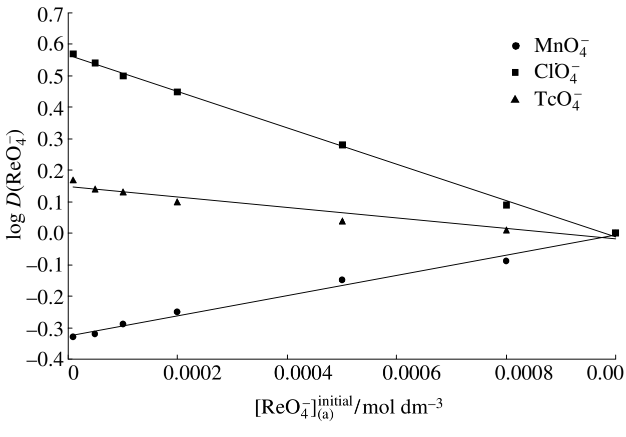

Figure 2 Mutual effect of oxo anions on the back extraction of 10^{-3} mol dm^{-3} tetraoctylammonium perrhenate into aqueous solutions of competing ions.

Data on the back extraction of ReO_4^- ions from tetraoctylammonium perrhenate solutions in nitrobenzene by a mixture of two oxo anions in the aqueous phase are shown in Figure 2. The abscissa illustrates the changes of the initial concentration of the perrhenate ion in the aqueous phase; hence, the concentration of the second oxo anion is 10^{-3} mol dm^{-3} at the zero point, it decreases with perrhenate concentration, and the total concentration of the oxo anions in the aqueous phase is kept equal to 10^{-3} mol dm^{-3}. As can be seen, all three regression lines meet together at the point where $\log D(ReO_4^-) = 0$.

In our opinion, different dependences of $\log D(ReO_4^-)$ on the initial concentration of perrhenate ions in the presence of second oxo anions result from the influence of two parameters, *i.e.*, the ratio of exchange constants and the ratio of dissociation constants. The MnO_4^- ion has the highest exchange constant, and the dissociation constant of its ion pair in nitrobenzene is higher than that of the perrhenate salt. Therefore, as the concentration of MnO_4^- in the aqueous phase increased, we observed a more effective back extraction of perrhenate ions into this phase. The exchange constants of ClO_4^- and ReO_4^- ions are close to one another; however, due to the higher dissociation constant of the ReO_4^- ion, its distribution ratio exceeds unity within the whole concentration range, though the back extraction line passes near to the abscissa. As to the back extraction by a mixture of TcO_4^- and ReO_4^- ions, we observed a transformation in the oxo anion selectivity. The exchange constant of the TcO_4^- ion is higher than that of ReO_4^- ion, but the dissociation constant of tetraoctylammonium perrhenate in nitrobenzene is approximately three times higher than that of the pertechnetate salt. This leads to the worse ability of the TcO_4^- ion to back extract ReO_4^- from a nitrobenzene solution of the QA salt.

The results allowed us to conclude that the dissociation of ion pairs in polar solvents takes place at the extraction of oxo anions by QA salts. Due to this effect, one can observe a mutual influence of oxo anions on the extraction and back extraction of one another. In our opinion, the reason for this is the influence of the common ion (the QA cation). The mutual effect of oxo anions is not so obvious as in the extraction of either metal-halide acids with oxygen-containing solvents or metal cations with macrocyclic compounds[10,11] because it is described by a greater number of parameters.

However, in practical applications of the above systems, for example, in the extraction of radionuclides from irradiated targets, it is necessary to consider the mutual influence of elements (*i.e.*, the so-called suppression of oxo anion extraction by another elements) because the distribution ratios of oxo anions, which are determined or calculated taking into account the presence of macrocomponents in a mixture, should be used for determining the separation and concentration ratios of radionuclides.

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