Extraction of oxoanions by tetraalkylammonium salts

Alexander A. Abramov,* Magomed S.-A. Dzhigirkhanov, Yurii I. Matyunin and Boris Z. Iofa

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 939 3187; e-mail: aaa@radio.chem.msu.ru

The extraction of MnO_4^-, TcO_4^-, RuO_4^- and RuO_4^{2-} from neutral and weakly alkaline solutions by tetraoctylammonium salts in benzene and toluene was studied by the slope method, and the concentration constants of the exchange of oxoanions for chloride and nitrate ions were estimated.

Information on the extraction of pertechnate, perrhenate, permanganate and perchlorate ions by tetraalkylammonium salts was published.[1–5] We failed to find data on the extraction of ruthenate and perruthenate ions by quaternary ammonium salts dissolved in hydrocarbons.

We studied the extraction of the above oxoanions by tetraoctylammonium nitrate and chloride in benzene and toluene. The results can be used for the separation and concentration of radionuclides, particularly, technetium and ruthenium isotopes.

Tetra-*n*-octylammonium bromide was synthesised using tri-*n*-octylamine and *n*-octyl bromide. The melting point was 94.5–95.5 °C; the bromide content was 99.3–99.7% (*cf.* ref. 6). Solutions of tetraoctylammonium chloride and nitrate were prepared by multiple exchange of 0.1 M tetraoctylammonium bromide with the solutions of NaCl and NaNO₃, respectively. Reagent-grade chemicals were additionally purified to remove reducing impurities. The distribution coefficients of technetium- and ruthenium-containing ions were determined radiometrically using the radioactive isotopes technetium-99 and ruthenium-106 in equilibrium with rhodium-106. Technetium-99 was measured on a Canberra Packard-2700 liquid-oscillation counter, and the radioactivity of ruthenium was detected from the equilibrium rhodium-106 using a γ-scintillation counter with a NaI (Tl) crystal. The distribution coefficients of manganese and the states of the oxoanions in aqueous and organic phases were determined spectrophotometrically on EPS-3T Hitachi and Shimadzu UV-3100 PC spectrophotometers.

Technetium solutions were prepared by dissolving technetium-99 metal (99.99%) in a mixture of nitric acid and hydrogen peroxide followed by evaporation and neutralization of the solution.

Table 1 Exchange constants of oxoanions with quaternary ammonium salts in benzene.

Anion	pH	Salt and its initial concentration in an aqueous phase/ mol dm⁻³	Extractant and its initial concentration in an organic phase/ 10⁴ mol dm⁻³	log K	z
MnO_4^-	7	KNO₃ 0.4–1.05	R₄NNO₃ 1.9–3.3	4.4±0.1	1.03±0.04
RuO_4^-	12.6	KMnO₄ (1.3–13.3)×10⁻⁴	R₄NMnO₄ 3.3–11	−0.5±0.02	1.08±0.06
RuO_4^-	—	KNO₃ 0.11–1.12	R₄NNO₃ 1.9–3.3	3.9±0.1	—
RuO_4^{2-}	0.9–4.0 M KOH	KCl (0.95–5)×10⁻³	R₄NCl 3–10.6	−0.43±0.08ᵃ	2.0±0.1
RuO_4^{2-}	—	—	R₄NNO₃	−4.43±0.08ᵇ	—
TcO_4^-	7–12	KNO₃ 0.1–0.5	R₄NNO₃ 5–10	3.6±0.1	0.98±0.04
ReO_4^-	7	LiNO₃ 0.001–1.0	R₄NNO₃ 0.1–1.0	3.08±0.07¹	—
ReO_4^-	7	LiClO₄ 0.001–1.0	R₄NClO₄ 0.1–1.0	0.11±0.04¹	—
ClO_4^-	7	—	R₄NNO₃	2.96±0.08ᶜ	—

ᵃToluene is the solvent. ᵇCalculated using published[1] and our data. ᶜCalculated using published[1] data.
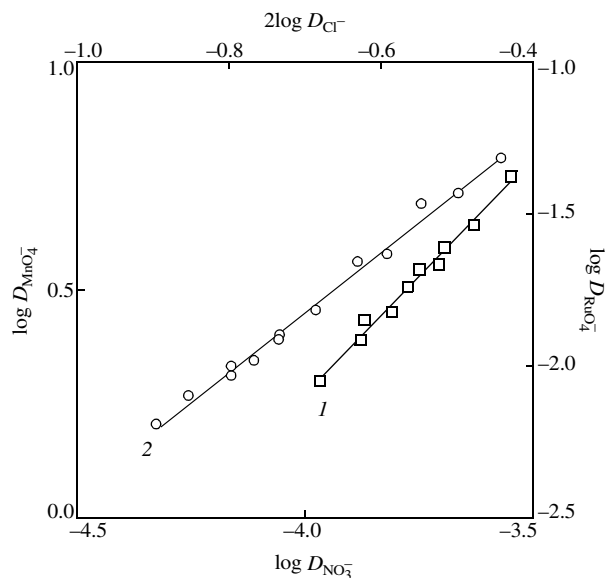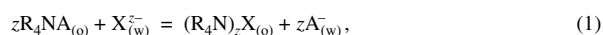

Figure 1 Distribution coefficients of (*1*) permanganate and (*2*) ruthenate ions *vs.* the distribution coefficients of nitrate and chloride ions, respectively.

Ruthenium metal (99.99%) was transformed into ruthenium dioxide. At this stage, a radioactive label was also introduced as ruthenium(IV) oxide. Then, ruthenium(IV) oxide was dissolved in a mixture of potassium hydroxide and hydrogen peroxide on heating, and potassium ruthenate solutions were obtained. Ruthenium(IV) was oxidised to perruthenate ions by a potassium hypochlorite solution.

To stabilise (hold) Ru^{7+} ions and to prevent their oxidation to RuO_4^- in aqueous solutions, the presence of KOCl and an alkali is required. Therefore, we used KRuO₄ (≤ 4×10⁻⁴ mol dm⁻³) solutions containing KClO (0.01 mol dm⁻³) and KOH (0.04 mol dm⁻³). The absorption spectra of aqueous and organic solutions suggest that MnO_4^- and RuO_4^- ions were not reduced during the extraction by the solutions of tetraoctylammonium nitrate in benzene, as well as RuO_4^{2-} ions were not reduced during the extraction by the alkaline solutions of tetraalkylammonium chloride in toluene. However, the above KRuO₄ solutions contained substantial amounts of Cl⁻, ClO⁻ and ClO₃⁻ anions. These anions are extracted into the organic phase together with RuO_4^- ions. Thus, it is difficult to determine the concentrations of NO₃⁻ ions in equilibrium organic and aqueous phases and the interphase exchange constants of RuO_4^-/NO_3^- ions. In this context, we investigated the extraction of RuO_4^- ions by tetraoctylammonium permanganate in benzene by spectrophotometrically measuring the MnO_4^- concentrations in equilibrium phases. At the same time, the exchange constant of RuO_4^-/NO_3^- ions was calculated by the method of combined ion-exchange equilibria.

The exchange reaction during the extraction of oxoanions is

$$z R_4NA_{(o)} + X_{(w)}^{z-} = (R_4N)_z X_{(o)} + z A_{(w)}^-, \qquad (1)$$

where $R_4NA_{(o)}$ is a teraalkylammonium salt; A⁻ is Cl⁻, NO₃⁻ or MnO_4^-; and X^{z-} is the extracted oxoanion. The subscripts (o) and (w) designate organic and aqueous phases, respectively.
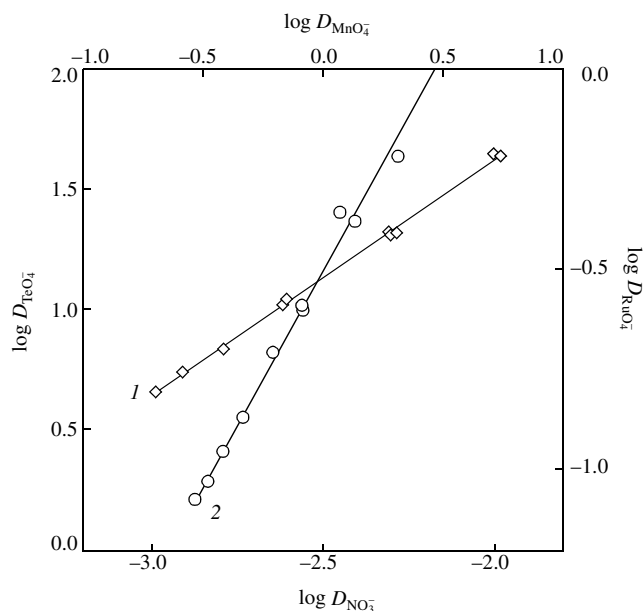
Figure 2 Distribution coefficients of (*1*) pertechnate and (*2*) perruthenate ions *vs.* the distribution coefficients of nitrate and permanganate ions, respectively.

The experimental distribution coefficients of oxoanions (*D*) are related to the exchange constant K_{X^{z-}/A^-} of reaction (1) by the equation

$$\log D_{X^{z-}} = \log K_{X^{z-}/A^-} + z\log \{[R_4NA]_{(o)}/[A^-]_{(w)}\} =$$
$$= \log K_{X^{z-}/A^-} + z\log D_{A^-} \quad (2)$$

Here, the equilibrium concentrations of the substances are given in parentheses.

Based on equation (2), experiments were performed to obtain $\log D_{X^{z-}}$ *vs.* $\log D_{A^-}$ relations for the studied X^{z-} ions. For this purpose, we changed the initial concentrations of R_4NA in the organic phase and the initial concentrations of the substituted anion A^- in the aqueous phase at the following fixed concentrations of ions: MnO_4^-, $(1–2)\times10^{-4}$; RuO_4^-, 1×10^{-5}; RuO_4^{2-}, $(6–7)\times10^{-5}$; TeO_4^-, 1×10^{-5} mol dm^{-3}.

In the experiments on RuO_4^{2-} extraction from alkaline solutions by R_4NA in toluene, we took into account two competitive

ion-exchange processes, *i.e.*, RuO_4^{2-}/Cl^- and OH^-/Cl^-, taking place in this extraction system. In this case, the D_{Cl^-} value was calculated from a material balance using the ion-exchange constant equal to 1.6×10^{-3} for the OH^-/Cl^- process in the system of R_4NCl in toluene.[7] The experimental $\log D_{X^{z-}}$ *vs.* $\log D_{A^-}$ relationships for the exchanging ions are shown in Figures 1 and 2. In terms of equation (2), we calculated the logarithms of exchange constants of oxoanions for the nitrate ion (Table 1). The logarithm of the ion-exchange constant for the RuO_4^-/NO_3^- system was calculated by the equation

$$\log K_{RuO_4^-/NO_3^-} = \log K_{MnO_4^-/NO_3^-} + \log K_{RuO_4^-/MnO_4^-}$$

The same approach, which took into account the value $\log K_{Cl^-/NO_3^-} = 2.0$ in the system with R_4NCl in toluene, was used for the calculations of $\log K_{RuO_4^{2-}/NO_3^-}$.[7]

Assuming that the substitution of tetraheptylammonium for tetraoctylammonium cannot substantially increase the exchange constants of these anions, we obtained the following order of selectivity (affinity) of monobasic oxoanions in the extraction by quaternary ammonium salts:

$$ClO_4^- < ReO_4^- < TcO_4^- < RuO_4^- < MnO_4^- .$$

The results allowed us to select the conditions for separating ruthenium and technetium radionuclides in the course of preparation from nuclear targets irradiated by charged particles.

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