371. *Solvent-extraction of Septivalent Rhenium. Part I. Heterogeneous Equilibria in the System, Aqueous Nitric Acid–Potassium Perrhenate–Tributyl Phosphate.*

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The extraction of septivalent rhenium into tributyl phosphate from aqueous nitric acid has been investigated as a function of solvent concentration in the organic, and nitric acid concentration in the aqueous phase, the rhenium concentration being kept constant. The method of continuous variations has been applied to follow the formation of the extractable rhenium compound. The results revealed that perrhenic acid was the only extractable species. The solvent-dependencies have been found to be of the direct fourth-power. The mass-action effect and the anti-synergic interaction between nitric and perrhenic acid have been used to interpret the extraction mechanism involved. An attempt has been made to calculate the formation constant of perrhenic acid tetrasolvate.

DURING work in this laboratory on solute–solvent interactions in heterogeneous ternary systems containing aqueous mineral acids and tributyl phosphate,[1] an attempt has been

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[1] (*a*) A. S. Kertes, *J. Inorg. Nuclear Chem.*, 1960, **12**, 377; **14**, 104; A. S. Kertes and V. Kertes, *Canad. J. Chem.*, 1960, **38**, 612; (*b*) *J. Appl. Chem.*, 1960, **10**, 287.

made to extract strong metal oxyacids. There have been relatively few attempts to investigate the extraction of metals in a high valency state, *e.g.*, those forming strong metal oxyacids of the type HMO_4, and it was hoped that distribution data on metals in the septivalent oxidation state would throw light on the behaviour of tributyl phosphate as extractant.

Most of the data [2] on the solvent-extraction of septivalent rhenium refer to determinations of rhenium(VII). It was shown that rhenium(VII) is extracted from strongly alkaline or neutral aqueous solutions by pyridine, piperidine, or ketones.[3] It is extracted from 2N-sulphuric acid by isopentyl alcohol, benzyl alcohol, hexahydronaphthalene, diethyl ketone, isobutyl methyl ketone, and tributyl phosphate, with distribution coefficients of 7, 5·8, 10·2, 3·7, 3·8, and 13·2 respectively. Tribalat [4] has also reported the extraction of perrhenic acid from highly acid solutions by ketones and alcohols. The highest distribution coefficients were obtained from sulphuric acid by using isopentyl alcohol.

EXPERIMENTAL

Reagents.—Commercial tributyl phosphate, from Commercial Solvents Corporation, was washed with sodium hydroxide solution and then six times with water, and the dissolved water was removed by distillation.[5] Baker's " Analysed c.p. " carbon tetrachloride was used as diluent without purification. The nitric acid solutions were prepared immediately before use from constant-boiling mixtures, thus eliminating contamination of more concentrated aqueous solutions with free nitrogen oxides. Potassium perrhenate was from Johnson, Matthey & Co. All other reagents used were of c.p. grade.

Equilibration and Phase Separation.—Portions (5 ml.) of standardized aqueous solutions containing various concentrations of nitric acid and potassium perrhenate were introduced into centrifuge tubes (10 ml. graduated in 0·1 ml.), and tributyl phosphate (5 ml.), with or without diluent, was added. The interface- and air-menisci were immediately noted. The stoppered tubes were then shaken, mechanically, equilibrium being shown to be reached in 15 min. Excellent phase separation was ensured by the use of tubes previously cleaned in sulphuric acid and one minute's centrifugation. The menisci at equilibrium were read with an accuracy of $\pm 0{\cdot}025$ ml. The average of at least three determinations, which never differed by more than 2%, was used in calculating the swelling of the organic phase due to the solubility in it of the aqueous solution. Aliquot parts of both phases were removed with a fine capillary pipette and diluted, the organic phase with a neutral water–ethanol mixture. Measurements were made at 20° ± 2°.

Analyses.—The acid content of the aqueous phase was determined potentiometrically in duplicate or triplicate by standard alkali, a Beckman Zeromatic pH-meter being used.

Potassium was determined in the equilibrated aqueous phase by using an EEL flame photometer. No interference was observed due to the presence of nitric acid or traces of tributyl phosphate in the solutions.

For determination of the low concentrations of nitrate ions use was made of the very sensitive reaction of nitrate with brucine.[6] To an aliquot part (5 ml.) of the nitrate solution were added a 2% brucine solution (0·5 ml.), concentrated sulphuric acid (10 ml.), and water (10 ml.). After the mixture had reached room temperature, the absorbance was measured on a Beckman model B spectrophotometer at 410 mμ. Neither perrhenate nor the ester interfered with this determination.

Perrhenate was determined only in aqueous solution, by the thiocyanate-reduction method.[7] Aliquot parts (0·5—1 ml.) were treated successively with concentrated hydrochloric acid (2 ml.), a 20% solution (0·1 ml.) of potassium thiocyanate, and 35% stannic chloride solution (0·15 ml.).

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[2] Tribalat, *Compt. rend.*, 1947, **224**, 469; *Ann. Chim. (France)*, 1949, 323; *Analyt. Chim. Acta*, 1952, **6**, 142; Miller, *J.*, 1941, 792.

[3] Gerlit, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, United Nations, 1956, Vol. VII, p. 145; Goishi and Libby, *J. Amer. Chem. Soc.*, 1952, **74**, 6109.

[4] Tribalat, " Rhénium et Technetium," Gautier-Villars Publ., Paris, 1957.

[5] Peppard, Driscoll, Sironen, and McCarty, *J. Inorg. Nuclear Chem.*, 1957, **4**, 326; Kennedy and Grimley, A.E.R.E., CE/R 968.

[6] Noll, *Ind. Eng. Chem. Analyt.*, 1945, **17**, 426.

[7] Tribalat, *Analyt. Chim. Acta*, 1949, **3**, 113.

After 15 min. rhenium was extracted from the resulting solution by isopentyl alcohol, and the absorbancy of the organic layer was measured at 435 mμ on the Beckman model B spectrophotometer. Excessive quantities of nitric acid were neutralized with calculated amounts of alkali without phenolphthalein, as originally indicated, because turbidity appeared on addition of the indicator. The method being very sensitive, freshly prepared and pure reagents were required. When less than 10^{-4} mole of rhenium was determined, interference was observed due to the presence of traces of tributyl phosphate in the equilibrated aqueous solutions. In these cases the traces of phosphate were removed by a preliminary extraction with carbon tetrachloride. This additional manipulation caused the limits of accuracy of these determinations to be double the normally estimated ±3%.

RESULTS AND DISCUSSION

Experiments were carried out with tributyl phosphate concentrations of 3·65M (undiluted), 3M, 2M, and 1·5M; the nitric acid concentration was varied between 0·1 and 8M, with a potassium perrhenate concentration of 10^{-3}M (except in the Job experiments). Preliminary experiments showed that perrhenate is not extracted in absence of nitric acid or when the concentration of this acid exceeds 8—9M, even when undiluted tributyl phosphate is used. With acid concentrations less than 0·1M or greater than 4M, and concentrations of tributyl phosphate in carbon tetrachloride less than 1·5M, the partition coefficient was too low for accurate estimation. The results obtained are presented in the Table.

Partition of rhenium(VII) *between aqueous nitric acid and tributyl phosphate.*

Initial $KReO_4$ concentration = 1 × 10^{-3}M.

		$[HNO_3]$ (M)			$[ReO_4]$ (10^{-5}M)		
Expt. no.	$[Bu_3PO_4]$ in CCl_4 (M)	Initial aq. soln. $[HNO_3]_i$	Equil. aq. phase $[HNO_3]_a$	Equil. org. phase $[HNO_3]_o$	Equil. aq. phase $[ReO_4]_a$	Equil. org. phase $[ReO_4]_o$	E_a° (ReO_4)
1	3·65	0·105	0·083	0·024	6·17	90·5	14·7
2	3·65	0·206	0·143	0·066	3·76	92·6	24·6
3	3·65	0·514	0·308	0·209	2·02	92·5	45·8
4	3·65	1·025	0·570	0·464	1·28	93·2	73·0
5	3·65	1·344	0·726	0·623	1·88	92·2	49·0
6	3·65	1·878	1·035	0·901	7·03	85·1	12·1
7	3·65	3·813	2·245	1·620	2·07	74·8	3·60
8	3·65	5·140	3·290	1·905	44·2	53·5	1·21
9	3·65	7·735	5·225	2·718	82·0	23·6	0·290
11	3·00	0·105	0·088	0·018	37·8	61·3	1·62
12	3·00	0·206	0·162	0·048	32·0	66·6	2·08
13	3·00	0·514	0·347	0·170	18·7	79·0	4·23
14	3·00	1·025	0·646	0·398	9·30	87·5	9·40
15	3·00	1·344	0·838	0·521	10·3	86·6	8·40
16	3·00	1·878	1·170	0·730	16·6	80·2	4·83
17	3·00	3·813	2·476	1·402	44·2	55·2	1·25
18	3·00	5·140	3·487	1·750	68·2	33·8	0·495
19	3·00	7·735	5·630	2·321	93·6	12·6	0·135
21	2·00	0·105	0·097	0·009	80·7	20·6	0·260
22	2·00	0·206	0·185	0·023	63·5	36·6	0·576
23	2·00	0·514	0·426	0·092	54·3	46·0	0·848
24	2·00	1·025	0·778	0·261	34·3	65·2	1·90
25	2·00	1·344	1·008	0·378	39·3	59·9	1·52
26	2·00	1·878	1·415	0·498	57·2	42·5	0·741
27	2·00	3·813	2·780	1·118	84·4	18·6	0·220
31	1·50	0·105	0·101	0·004	90·6	6·31	0·071
32	1·50	0·206	0·198	0·009	89·1	11·4	0·127
33	1·50	0·514	0·461	0·058	81·9	19·3	0·236
34	1·50	1·025	0·866	0·171	81·1	20·1	0·248
35	1·50	1·344	1·099	0·281	76·7	24·3	0·317
36	1·50	1·878	1·535	0·377	88·4	11·6	0·131

For study of the equilibrium between the acid and perrhenate in the aqueous phase, Job's method of continuous variations was used.[8] The concentration of phosphate in the diluent was kept constant, at 3M, and that of total electrolytes (potassium perrhenate and nitric acid) at 0·036M. The aqueous electrolyte concentration was chosen as being almost the highest possible for aqueous solutions of potassium perrhenate. A graph of $[ReO_4]_o$, the rhenium content of the organic phase, against the molar composition of the components in the aqueous phase (Fig. 1) shows an extremum at a molar $HNO_3:KReO_4$ ratio of unity. At this ratio neither nitrate nor potassium ions were present in the organic phase. Potassium could not be detected in either of the organic phases. Nitrate appeared in the organic phase only when rhenium was not present in the aqueous phase or when the molar $HNO_3:KReO_4$ ratio was 9 : 1. The linear relation in the upward branch of the curve, and the consequent sharpness of the peak, indicate further that perrhenic acid must be the only extractable septivalent rhenium species and that the resulting perrhenic acid–phosphate solvate must have considerable stability. Perrhenate is not-extracted in absence of acid but, on the other hand, the perrhenate extraction inhibits the extraction of nitric acid when both are present in equimolar, or nearly equimolar, ratios.

The $HNO_3:KReO_4$ ratio of unity in the formation of the extractable species is confirmed by a log–log plot of E_a° against nitric acid concentration in the equilibrium aqueous phase. Fig. 2 shows this plot for the different concentrations of tributyl phosphate used in this study. Independently of the phosphate content of the organic phase, the distribution ratio increases with increasing acidity in the aqueous solution up to a maximum value at about M-nitric acid in the equilibrated aqueous phase. The slope of unity of the branches showing increases indicates a $HNO_3:KReO_4$ ratio of unity, and the dependence of E_a° on the hydrogen-ion concentration proves that the extracting species must be a strong acid, identified as free perrhenic acid.

The solvation number of perrhenic acid was found by the slope of a log–log plot of E_a° against the concentration of tributyl phosphate in the initial organic phase at constant nitric acid concentrations. The straight lines in Fig. 3, representing this graph, show a slope of ~4 for all the acid concentrations used, suggesting that a tetrasolvate of perrhenic acid exists in the tributyl phosphate phase. Although use of arguments of this type for the determination of the solvation number may be criticised[9] when high tributyl phosphate concentrations are used, we believe that the present results are not misleading. The identical solvation number of four, recently revealed for perchloric acid, a very similar molecule to perrhenic acid, can be cited as a further argument for the existence of perrhenic acid tetrasolvate. Kertes and Kertes,[1b] and Fomin and Maiorova,[10] from completely different experiments, deduced the existence of a complex $HClO_4,4(Bu_3PO_4)$ in the organic phase.

An attempt has been made to calculate the equilibrium constant of the reaction

$$4Bu_3PO_4(org.) + H^+(aq.) + ReO_4^-(aq.) \rightleftharpoons HReO_4(Bu_3PO_4)_4(org.)$$

$$K = [HReO_4(Bu_3PO_4)_4]_o/[Bu_3PO_4]_o[H^+]_a[ReO_4^-]_a$$

taking into account the degree of ionization of nitric acid[11] and identifying $[HReO_4(Bu_3PO_4)_4]_o$ with $[ReO_4]_o$, the concentration of rhenium in the organic phase. Free tributyl phosphate (*i.e.*, the portion not engaged in the complex) was calculated by assuming complete formation of the nitric acid monosolvate[12] HNO_3,Bu_3PO_4. The constants calculated varied between 0·55 and 0·11, with an average of 0·21. Several of the values diverge drastically from the mean value, especially at high phosphate and

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[8] Cf. Irving and Pierce, *J.*, 1960, 2565; Specker, Cremer, and Jackwerth, *Angew. Chem.*, 1959, **71**, 492; Jackwerth and Specker, *Z. analyt. Chem.*, 1959, **168**, 340.

[9] Cf. Hesford and McKay, *Trans. Faraday Soc.*, 1958, **54**, 573.

[10] Fomin and Maiorova, *Zhur. neorg. Khim.*, 1960, **5**, 1100.

[11] Young, Maranville, and Smith, in "The Structure of Electrolytic Solutions," ed. W. J. Hamer, John Wiley & Sons, New York, 1959, p. 42.

[12] Tuck, *J.*, 1958, 2783; Alcock, Grimley, Healy, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.

low nitric acid concentrations. Fomin and Maiorova [10] reported a mean value of 0·16 for the formation constant of the perchloric acid tetrasolvate, the variation being 0·12—0·20. The value of this constant is very near to our value of 0·21 for $HReO_4,4Bu_3PO_4$.

The first main factor influencing the system under consideration is the similarity of the two extracting species HNO_3 and $HReO_4$, the distribution of which between the two phases depends on their concentration and on the degree of dissociation of the two compounds containing an ion in common. The ratio of the only extractable species (undissociated $HReO_4$ to undissociated HNO_3) in the aqueous phase should be governed by mass-action effect, depending on the strength of the two acids. For the time being no quantitative interpretation of the mass-action effect can be offered, but in our opinion the differences in the acid-to-extractant affinities and the difference in their solvation number are not alone sufficient to explain the extraction mechanism involved.

Fig. 1. *Plot of the rhenium content of the organic phase,* $[ReO_4]_o$, *against the molar composition of the initial aqueous solutions in experiments of Job's method of continuous variations.*

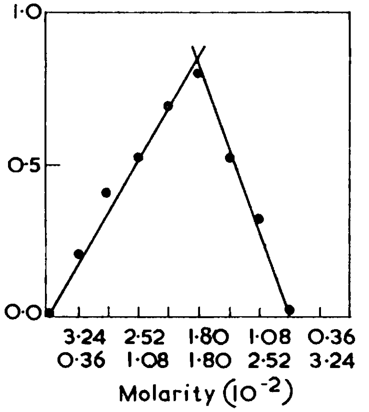
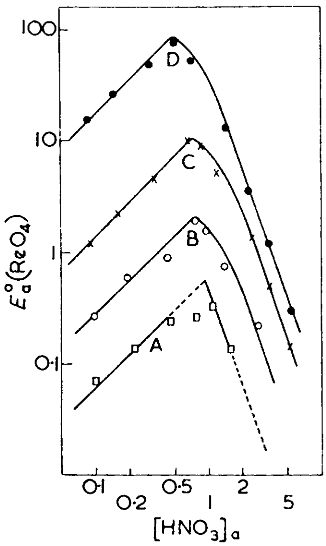


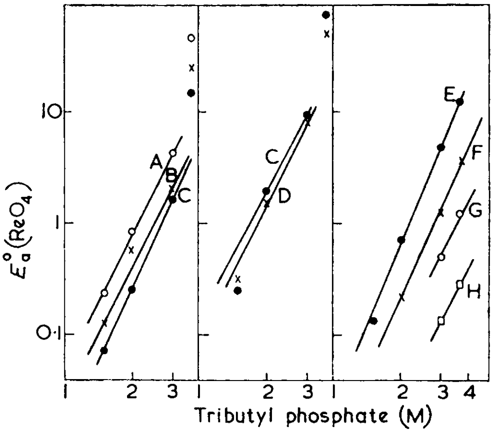
Fig. 2. Log–log *plot of the rhenium extraction ratio* $E_a^\circ(ReO_4)$ *against hydrogen-ion concentration in the equilibrated aqueous phases.*



Molarity of tributyl phosphate: A, 1·5; B, 2·0; C, 3·0; D, 3·65.

Fig. 3. Log–log *plot of the rhenium extraction ratio,* $E_a^\circ(ReO_4)$, *against tributyl phosphate concentration in the organic phase for various initial nitric acid concentrations.*

Molarity of nitric acid: A, 0·514; B, 0·206; C, 0·105; D, 1·344; E, 1·878; F, 3·813; G, 5·140; H, 7·735.



The increase in amount of perrhenic acid in the organic phase at low nitric acid concentration, and its decrease at higher nitric acid concentrations, may be explained roughly by the competition between the two acids for the available tributyl phosphate. One would expect the formation of higher solvates to be favoured when the concentration of tributyl phosphate is much greater than that of the extractable nitric and perrhenic acid.

The progressive uptake of nitric acid by the phosphate results in the formation of lower perrhenic acid solvates, a phenomenon consistent with previous findings in extraction equilibria.[9] It seems, therefore, that all the rhenium compounds containing less than four mol. of tributyl phosphate have a smaller tendency to remain in the organic phase than has the stable monosolvate of nitric acid,[12] thus forcing the rhenium out of the organic phase.

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