

METALLIC NITRATES IN PAPER CHROMATOGRAPHY

III. THE SYSTEM DI-ISOPROPYL ETHER-NITRIC ACID-WATER

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This paper presents further results^{1,2} on the chromatographic behaviour of metallic nitrates in organic solvents usually used in processes of extraction in radiochemistry. The purpose of this study was to determine the extent to which nitric acid is distributed between the aqueous and di-isopropyl ether phases and to consider the possible effects which this distribution has on the R_F values of metallic nitrates in the system involved.

Early research in solvent extraction disclosed that some metallic species are well extracted from aqueous phases into organic solvents and that some show very low or zero extractability. In practice, the choice of the organic solvent depends upon its selectivity in a desired separation. Di-isopropyl ether is one of the solvents investigated and used in the solvent extraction of fissile and fertile materials³. In recent years, it has been very widely used for the extraction of ferric chloride from aqueous solutions containing various concentrations of hydrochloric acid⁴ and hydrochloric acid together with other chlorides serving as salting-out agents⁵. The distribution of radiogallium⁶ and radioiron⁷, and of tri- and pentavalent antimony⁸ between aqueous hydrochloric acid and the solvent has been determined. The optimum conditions for the extraction of inorganic chlorides from aqueous hydrochloric acid solutions of varying concentrations have also been studied⁹. Gold has been separated by the extraction technique from group VIII elements using the hydrobromic acid-isopropyl ether system¹⁰. Ceric, thorium and scandium nitrates have been successfully extracted and separated from some other inextractable nitrates in aqueous nitric acid solution using this solvent¹¹.

Isopropyl ether has found some application in adsorption chromatography, and also to a lesser degree in paper chromatography, for the separation of antimony from tin¹².

EXPERIMENTAL

The di-isopropylether (DIPE), also known as isopropyl ether $(\text{CH}_3)_2\text{CH}\cdot\text{O}\cdot\text{CH}\cdot(\text{CH}_3)_2$, was a pure commercial product supplied by Shell. As purchased, it may contain, in common with ethers, peroxides formed through contact with air and exposure to light. The peroxides were removed by washing followed by distillation from an all-glass

Pyrex apparatus, only the middle fraction being retained for use. Immediately before use the ether was tested for the absence of peroxides by the potassium iodide test.

DIPE is soluble to the extent of 1.07% by weight in water, which itself is soluble in the compound up to 0.53% at 20°. The specific gravity at (20°/4°) is 0.7238. The boiling point at 760 mm Hg is 68.5° and the distillation range of 65–70° meets ASTM specifications.

The initial aqueous solutions were prepared by diluting a freshly boiled non-fuming nitric acid stock solution (approximately 14 *M*) with water. The experimental technique of equilibrating the aqueous and etheric phases and of determining the acid content of the phases was similar to the procedure given in previous parts^{1,2} of this series. The changes in volume after shaking equal volumes of the two phases were measured in three parallel experiments using graduated, glass-stoppered cylinders of 10, 25 and 50 ml capacity, graduated at 0.1, 0.2 and 0.5 ml respectively. Very good agreement was obtained in three parallel determinations, thus excluding the necessity of averaging the results.

The chromatographic experiments were carried out according to the methods and procedures described in previous publications¹³. Radioactivity measurements were carried out using a mica end-window counter for soft β -rays employing a technique described elsewhere¹⁴.

The working temperature was 22–25°.

RESULTS

Distribution of nitric acid

Table I shows the composition of the initial aqueous solutions, the molar concentrations of nitric acid in the aqueous and organic layers, as well as the calculated concen-

TABLE I
THE DISTRIBUTION OF NITRIC ACID BETWEEN WATER AND DI-ISOPROPYL ETHER

No. of solution	Concentration of HNO ₃ moles/l			V _o /V _w	α	μ
	in the initial solution	in the aqueous layer	in the organic layer			
1	2	3	4	5	6	7
1	0.070	0.069	0.001	1.00	0.012	0.012
2	0.344	0.339	0.003	1.00	0.009	0.009
3	0.685	0.667	0.012	1.00	0.018	0.018
4	1.379	1.327	0.050	1.00	0.038	0.038
5	2.071	1.939	0.129	1.00	0.066	0.066
6	2.770	2.493	0.251	1.00	0.101	0.101
7	4.168	3.463	0.667	1.00	0.193	0.193
8	5.526	4.372	1.282	1.08	0.293	0.316
9	7.197	5.315	2.229	1.22	0.419	0.512
10	8.943	6.438	3.118	1.37	0.484	0.663
11	10.839	8.002	3.970	1.54	0.496	0.772
12	12.642	9.288	4.734	1.69	0.510	0.862

TABLE II
 R_F VALUES OF IONS OBTAINED IN DI-ISOPROPYL ETHER SATURATED
 WITH VARIOUS CONCENTRATIONS OF AQUEOUS NITRIC ACID SOLUTION

Ionic solution	Number of solvent*									
	2	3	4	6	7	8	9	10	11	12
$\text{UO}_2(\text{NO}_3)_2$	0.00	0.01	0.03	0.11 t	0.24 t	0.70 t	1.00	1.00	1.00	1.00
$\text{Th}(\text{NO}_3)_4$	0.00	0.00	0.00	0.00	0.00	0.07	0.20	0.20	0.20	0.20
SbCl_3	0.01	0.01	0.02	0.06	0.11	0.24	0.31	0.37	0.36	0.40
SnCl_2	0.00	0.00	0.00	0.01	0.02	0.03	0.03	0.03	0.03	0.03
AsCl_3	0.00	0.00	0.00	0.00	0.03	0.02	0.03	0.02	0.02	0.06
AuCl_3	0.19 t	0.19 t	0.29 t	0.92 t	1.00	1.00	1.00	1.00	1.00	1.00
PdCl_2	0.21 t	0.22 t	0.30 t	0.50 t	1.00	1.00	1.00	1.00	1.00	1.00
AgNO_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.08
KI	0.00	0.00	0.31 t	0.42 t	0.63 t	1.00	1.00	1.00	1.00	1.00
KReO_4	0.00	0.00	0.00	0.00	0.06	0.18	0.30	0.30	0.28	0.23
Na_2SeO_3	0.00	0.00	0.00	0.00	0.00	0.06	0.17	0.33	0.40	0.00
$\text{Na}_2\text{B}_4\text{O}_7$	0.01	0.02	0.02	0.02	0.03	0.04	0.09	0.03	0.00	0.00
OsO_4	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

* Compare the composition of the solution in Table I.
 t = tailing.

tration and mass-distribution coefficients as defined previously². Column 5 gives the ratios of the volumes (after equilibration) of the etheric and aqueous layers.

Reaction of the ether with nitric acid

In the extraction of nitric acid at high concentrations, over 8 *M*, into DIPE, a considerable amount of the acid passes over into the etheric layer, as can be seen from Table I. It was observed that such organic solutions were rather unstable, undergoing violent reaction with the liberation of nitrogen oxides. These reactions were similar to those observed with methyl isobutyl ketone^{1, 15}. The time required for this reaction in the separated etheric layer depended on the acid concentration. When the aqueous phase contained 8 *M* nitric acid, the etheric phase underwent reaction after 24 h; 10 *M* nitric acid reacted after approximately half the above time and a 12 *M* solution after only a few hours. It was impossible to mix a 14 *M* or more concentrated aqueous solution of nitric acid with DIPE, because of the violent and instantaneous reaction with the ether.

Paper chromatographic experiments

The great majority of the ions investigated showed R_F values equal to zero, whatever the nitric acid concentration. The R_F values of those ions which moved on the paper are presented in Table II. R_F values of zero were obtained for the following elements spotted on filter paper as:

$\text{Ba}(\text{NO}_3)_2$	$\text{Pb}(\text{NO}_3)_2$	$\text{Bi}(\text{NO}_3)_3$	GeF_4
$\text{Sr}(\text{NO}_3)_2$	$\text{Hg}(\text{NO}_3)_2$	$\text{In}(\text{NO}_3)_3$	NbF_5
$\text{Ca}(\text{NO}_3)_2$	$\text{ZrO}(\text{NO}_3)_2$	$\text{Ga}(\text{NO}_3)_3$	TaF_5
$\text{Mg}(\text{NO}_3)_2$	CsCl	$\text{Y}(\text{NO}_3)_3$	PtH_2Cl_4
$\text{Be}(\text{NO}_3)_2$	RbCl	$\text{La}(\text{NO}_3)_3$	$^{106}\text{Ru}(\text{NO}_3)_3$

Cu(NO ₃) ₂	KNO ₃	¹⁴⁴ Ce(NO ₃) ₃	RhCl ₃
Co(NO ₃) ₂	TiNO ₃	Nd(NO ₃) ₃	TiCl ₃
Ni(NO ₃) ₂	Tl(NO ₃) ₃	Pr(NO ₃) ₃	VCl ₃
Cd(NO ₃) ₂	Al(NO ₃) ₃	Sm(NO ₃) ₃	TeO ₃ Na ₂
Mn(NO ₃) ₂	Cr(NO ₃) ₃	Gd(NO ₃) ₃	WO ₄ Na ₂
Zn(NO ₃) ₂	Fe(NO ₃) ₃	Ce(NO ₃) ₄	MoO ₄ (NH ₄) ₂
		¹⁶⁰ Tb(NO ₃) ₃	

Chromatograms were run in DIPE saturated with the higher concentrations of nitric acid after the solvent had decomposed. The great majority of the ions which showed zero R_F values in non-reacted DIPE solution, gave high R_F values in these solutions. These values were not reproducible. It is very likely that in cases where the acid content in the eluant is high and therefore there is a great probability of numerous reactions between the acid and the ether, the R_F values cannot be attributed to the nitric acid-ether mixtures, but are in part dependent on the various products formed between nitric acid and the di-isopropyl ether.

DISCUSSION

Comparing the R_F values obtained in this study with those obtained previously¹ using methyl isobutyl ketone (MIBK) instead of DIPE, some basic differences are immediately obvious. Uranyl nitrate gave R_F values of unity in MIBK saturated with 3 M nitric acid, whilst for the same extraction using DIPE an approximately 7 M nitric acid solution is needed. Thorium nitrate also showed higher R_F values in the ketone. The same is true for antimony, tin and arsenic. Generally speaking, MIBK extracted the extractable metallic nitrate species more economically with a lower nitric acid concentration level. Zirconyl and mercuric nitrates gave zero R_F values in DIPE, but in the MIBK system both gave R_F values, the value for mercuric nitrate being quite high. The behaviour of the two last-mentioned nitrates seems to be rather important. Zirconyl, being a fission product, is present in fuels and mercury often serves as a good catalyst for the dissolution of the metallic fuel—the dissolution rate is increased by a factor of 10 when mercuric nitrate is added to the nitric acid solution¹⁰. In contrast to

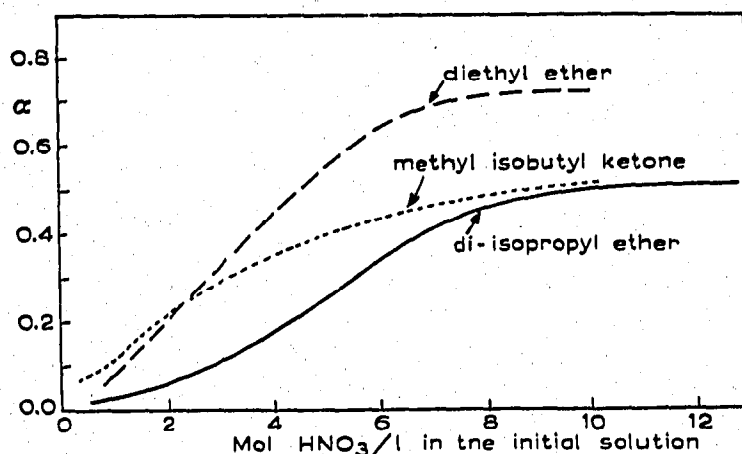


Fig. 1. The distribution coefficient of nitric acid between water and organic solvents as a function of the nitric acid concentration in the initial aqueous solutions.

DIPE, which as is shown here, does not extract mercuric nitrate, MIBK when used in extraction processes after radiochemical separations must extract mercuric nitrate together with the uranium, according to our previous experiments¹.

In Fig. 1 are plotted the distribution coefficients of nitric acid between water/MIBK and water/DIPE versus the molar concentration of nitric acid in the initial aqueous solution. As can be seen, a higher percentage of nitric acid is extracted into MIBK than into DIPE. On studying the influence of lithium nitrate as a salting-out agent upon the R_F values of extractable metallic nitrates², it was found that the R_F values of some (uranyl, mercury and gold) ions are a function of the total nitrate ion concentration in the organic phase, which serves as the eluant in paper chromatography. As was pointed out above, in order to achieve the same extractability (the same R_F value) of a given metallic nitrate, less nitric acid is needed in the MIBK system than in the DIPE system, in accordance with higher extractability of the nitric acid into MIBK compared with its extractability into DIPE, as is seen from Fig. 1.

For comparison the distribution curve of nitric acid between water and diethyl ether as determined by BOCK AND BOCK¹¹ is given. On the basis of the above observation it may be predicted that R_F values in diethyl ether should be higher at the same nitric acid concentration level (or the same R_F value for a given metallic nitrate should be reached in diethyl ether with less nitric acid in the initial solution) than in the MIBK and DIPE systems.

SUMMARY

The distribution of nitric acid between water and di-isopropyl ether has been studied for various concentrations of the acid. Chromatograms of 58 ions were run in solvent mixtures of the ether and various concentrations of the acid. The great majority of the ions tested gave zero R_F values. The results were compared with those obtained previously in similar systems containing methyl isobutyl ketone instead of di-isopropyl ether.

REFERENCES

- ¹ A. S. KERTES, *J. Chromatol.*, 1 (1958) 62.
- ² A. S. KERTES AND A. H. I. BEN-BASSAT, *J. Chromatol.*, 1 (1958) 489.
- ³ F. R. BRUCE, *Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, Paper No. P/719; F. L. CULLER, *ibid.*, No. P/822.
- ⁴ N. H. NACHTRIEB AND I. G. CONWAY, *J. Am. Chem. Soc.*, 70 (1948) 3547; N. H. NACHTRIEB AND R. E. FRYXELL, *ibid.*, 70 (1948) 3552; R. W. DODSON, G. I. FORNEY AND E. H. SWIFT, *ibid.*, 58 (1936) 2573; R. I. MYERS, D. E. METZLER AND E. H. SWIFT, *ibid.*, 72 (1950) 3767; S. D. CAVERS, *Nuclear Sci. Abstr.*, 7 (1953) 5739.
- ⁵ A. H. LAURENE, *Nuclear Sci. Abstr.*, 7 (1953) 3037.
- ⁶ N. H. NACHTRIEB AND R. E. FRYXELL, *J. Am. Chem. Soc.*, 71 (1949) 4035.
- ⁷ G. I. VOSBURGH, L. B. FLEXNER AND D. B. COWIE, *J. Biol. Chem.*, 175 (1948) 391.
- ⁸ F. C. EDWARDS AND A. F. VOIGT, *Anal. Chem.*, 21 (1949) 1204.
- ⁹ D. E. CAMPBELL AND A. H. LAURENE, *Nuclear Sci. Abstr.*, 6 (1952) 3766.
- ¹⁰ W. A. E. MCBRYDE AND I. H. YOE, *Anal. Chem.*, 20 (1948) 1094.
- ¹¹ R. BOCK AND E. BOCK, *Z. anorg. u. allgem. Chem.*, 263 (1950) 146.
- ¹² F. H. BURSTALL, G. R. DAVIES, R. P. LINSTAD AND R. A. WELLS, *J. Chem. Soc.*, (1950) 516.
- ¹³ S. KERTES AND M. LEDERER, *Anal. Chim. Acta*, 15 (1956) 543; R. G. DE CARVALHO, *ibid.*, 16 (1957) 555.
- ¹⁴ S. KERTES AND M. LEDERER, *Anal. Chim. Acta*, 16 (1957) 40.
- ¹⁵ L. E. GLENDENIN, K. F. FLYNN, R. F. BUCHANAN AND E. P. STEINBERG, *Anal. Chem.*, 27 (1955) 59.
- ¹⁶ R. G. WYMER AND D. L. FOSTER, *Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, Paper No. P/547.

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