METALLIC NITRATES IN PAPER CHROMATOGRAPHY

II. THE SYSTEM METHYL ISOBUTYL KETONE–NITRIC ACID–LITHIUM NITRATE–WATER

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In continuation of a recent report[1] on the chromatographic behaviour of metallic nitrates in the system methyl isobutyl ketone(MIBK)–nitric acid–water, we have now studied the distribution of nitric acid and lithium nitrate between water and MIBK, and have measured the R_F values of 55 ions in the above mixtures.

A chromatographic study of a large number of ions in one given solvent system may yield numerous useful separations. The R_F values obtained for cations may to a certain extent be related to the distribution coefficients for the same cations obtainable by the extraction technique in the same solvent system. This relationship is rather imperfect, amongst other things, because of the influence of the solvent itself, and of its water and acid content, upon the cellulose and because of the changes in solvent composition that occur during the development of the chromatograms. Thus, a chromatographic study can serve only as a preliminary, but it may provide a basis for possible separations of macro quantities by the extraction technique. With this aim in mind, it appeared necessary and important to carry out a systematic and detailed study of the solvent system itself. Up to the present no attention has been paid to the exact composition of the eluants used in paper chromatography: the distribution of acids, salting-out agents and complexing agents between the aqueous and organic layers has never been determined. A study of this problem should permit a more fundamental interpretation of the R_F values obtained, and in certain cases is likely to serve as a basis for some theoretical considerations.

In radiochemical processes where the dissolution of the fuel is generally carried out with nitric acid, inorganic nitrates are often added to the nitric acid to increase the dissolution rate of the uranium[2]. Sometimes nitrates appear more promising than nitric acid as aqueous salting-out agents in the solution from which the extraction is to be made. Experiments have often shown[3,4] that a much higher partition coefficient is obtained when part of the nitric acid in the aqueous phase is replaced by neutral inorganic nitrates, which themselves are practically insoluble in the organic phase[5]. In the case of extraction with MIBK, the partition coefficient of the extractable species is dependent both on the concentration of nitric acid and of the nitrates in the aqueous phase[6]. The same was found for R_F values in paper chromatography[1]. It is often sufficient to add nitrates to obtain the necessary salting-out strength without

making the aqueous phase highly acidic. Nitrates with low equivalent weight of the cation, like lithium and magnesium nitrates, were found to be especially useful as salting-out agents[4].

The effects of salts have also been examined in inorganic paper chromatography[7]. The technique employed was impregnation, *i.e.* dipping the paper in salt solution and drying before chromatography. The salting-out effect on uranyl nitrate was found to be identical with that observed in solvent extraction[7]. LEDERER[8] made a comparison of R_F values for several cations on both unimpregnated and sodium chloride-impregnated paper in butanol saturated with N hydrochloric acid. Nitric acid is rarely employed as an eluant in paper chromatography, since the nitrate-complexing of metals is usually small. MIBK does not belong to the organic solvents widely used in paper chromatography and only isolated reports of its use were found in the literature[9].

EXPERIMENTAL

Methyl isobutyl ketone was a "Shell" pure commercial product and was distilled before use from an all-glass Pyrex still; only the middle fraction (114–117°) was retained. "Baker's Analyzed" nitric acid and lithium nitrate were employed.

Initial aqueous solutions, containing varying amounts of nitric acid and lithium nitrate, were prepared by taking aliquots of concentrated non-fuming nitric acid and aliquots of a 6 M lithium nitrate stock solution. Equal volumes of these aqueous solutions and the MIBK were equilibrated at room temperature using the procedure described previously[1]. The changes in volume after equilibration were followed using graduated (0.5 ml) glass-stoppered cylinders; the readings were made with an accuracy of ± 0.25 ml, the relative error being ± 0.5%. The distribution of nitric acid between

TABLE I

THE DISTRIBUTION OF NITRIC ACID AND LITHIUM NITRATE BETWEEN WATER AND METHYL ISOBUTYL KETONE

No. of solution	Moles/l in initial solution		V_0/V_w	HNO_3		$LiNO_3$	
	HNO_3	$LiNO_3$		a	μ	a	μ
1	2	3	4	5	6	7	8
1	1.006	0.212	1.00	0.135	0.135	0.0037	0.0037
2	1.011	0.558	1.00	0.185	0.185	0.0018	0.0018
3	0.996	1.078	1.00	0.281	0.281	0.0015	0.0015
4	1.011	2.260	1.04	0.548	0.571	0.0022	0.0023
5	1.001	3.261	1.06	0.953	1.008	0.0037	0.0039
6	1.006	4.314	1.08	1.574	1.700	0.0053	0.0057
7	0.996	6.300	1.10	3.381	3.719	0.0085	0.0093
8	0.506	1.075	1.00	0.216	0.216	0.0012	0.0012
9	0.996	1.078	1.00	0.281	0.281	0.0015	0.0015
10	2.017	1.076	1.04	0.402	0.418	0.0040	0.0042
11	3.006	1.095	1.09	0.458	0.499	0.0103	0.0112
12	4.001	1.061	1.17	0.512	0.599	0.0288	0.0337
13	6.001	1.065	1.33	0.562	0.747	0.0491	0.0652
14	8.002	1.087	1.53	0.585	0.895	0.0585	0.0895

water and MIBK was determined potentiometrically using a Beckman Model H2 pH-meter. The aqueous phases were titrated with aqueous sodium hydroxide, and the organic phases with ethanolic sodium hydroxide, the latter being standardized against ethanolic benzoic acid solution. The lithium nitrate content of the phases was measured using an EEL flame photometer. The total amounts of both nitric acid and lithium nitrate found differed from the amounts in the initial aqueous solution by a maximum of $\pm$ 1%. In Expts. 5, 6 and 7 in Table I, the lithium nitrate total was outside this limit of error, apparently because the high concentration of the salt required a dilution of 1:10,000, which was bound to involve considerable error.

The technique and procedure for the chromatographic experiments, the reagents and methods for detection of the spots have been described in previous papers[10].

The working temperature was 23–25°.

<div align="center">RESULTS</div>

Two sets of experiments were carried out. In the first set, Nos. 1 to 7, the original aqueous solution contained a constant amount of nitric acid and the lithium nitrate concentration was varied. In the second set, Nos. 8 to 14, the lithium nitrate concentration in the initial aqueous solution was kept constant and the nitric acid concentration varied. The exact composition of the initial aqueous solution is given in Table I, columns 2 and 3, for nitric acid and lithium nitrate respectively.

The distribution of the salting-out agents, nitric acid and lithium nitrate between the aqueous and organic layers is presented as the concentration distribution coefficient a

$$a = \frac{\text{concentration of salting agent in the organic layer (moles/l)}}{\text{concentration of salting agent in the aqueous layer (moles/l)}}$$

and as the mass distribution coefficient μ, defined as

$$\mu = \frac{\text{total amount of salting agent in the organic layer}}{\text{total amount of salting agent in the aqueous layer}}$$

The relation between these two units is given by $\mu = (V_o/V_w)a$ where V_o and V_w represent the volumes (after equilibration) of the organic and of the aqueous layers respectively. The values for the ratio V_o/V_w are given in column 4 of Table I.

The calculated coefficients for both nitric acid and lithium nitrate are presented in Table I. As can be seen from the values in columns 5 and 6, the solubility of nitric acid in the MIBK layer is greatly influenced by the concentration of lithium nitrate present in the initial aqueous solution. The inorganic nitrate is an excellent salting-out agent for nitric acid[11]: the distribution coefficient of nitric acid increases on increasing the amount of lithium nitrate in the initial aqueous solution. About 12% of the total nitric acid is extracted into the organic layer when the molar ratio of nitric acid to lithium nitrate is approximately 5:1; when this ratio is about 1:5 the amount of nitric acid extracted reaches 75%. On increasing the molarity of the nitric acid in the initial solution from 0.5 to 8 M (Expts. 8–14), the nitric acid extracted increases roughly from 20% to 40%.

TABLE II

R_F VALUES OF IONS IN METHYL ISOBUTYL KETONE EQUILIBRATED WITH AQUEOUS SOLUTIONS
CONTAINING VARIOUS AMOUNTS OF NITRIC ACID AND LITHIUM NITRATE

Ionic solution	Number of solvent*													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Th(NO$_3$)$_4$	0.01	0.02	0.03	0.07	0.15 t	0.25 t	0.39 t	0.02	0.03	0.20 t	0.20	0.30	0.50 t	0.73 t
ZrO(NO$_3$)$_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.08 t	0.19 t
UO$_2$(NO$_3$)$_2$	0.28	0.43	0.49	0.61	0.78	0.88	0.94	0.41	0.49	0.75	1.00	1.00	1.00	1.00
Hg(NO$_3$)$_2$	0.69	0.73	0.73	0.76	1.00	1.00	1.00	0.73	0.73	1.00	1.00	1.00	1.00	1.00
Bi(NO$_3$)$_3$	0.02	0.02	0.02	0.02	0.03	0.04	0.06	0.01	0.02	0.04	0.06	0.07	0.08	0.09
SbCl$_3$	0.14	0.22	0.23	0.28	0.36	0.52	0.63	0.23	0.23	0.44	0.57	0.75	0.88	0.94
SnCl$_2$	0.32	0.33	0.36	0.44	0.50	0.54	0.72	0.33	0.36	0.46	0.49	0.51	0.50	0.47
AsCl$_3$	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.02	0.02	0.02	0.03	0.05	0.06	0.10
AuCl$_3$	0.43	0.45	0.50	0.59	0.70	0.77	0.82	0.41	0.50	0.72	0.91	1.00	1.00	1.00
Na$_2$SeO$_3$	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.03	0.03	0.05	0.09
NaI	0.19 t	0.25 t	0.29 t	0.60 t	0.64 t	0.69 t	0.88	0.16 t	0.29 t	0.69 t	0.93	1.00	1.00	1.00
Na$_2$B$_4$O$_7$	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.07	0.08	0.12	0.15

* Compare the composition of the aqueous solution in Table I.

t = tailing.

As is known, lithium nitrate is only very sparingly soluble in the organic layer. By increasing the molarity of the salt in the initial aqueous solution from 0.2 to 6.5 M (Expts. 1–7), the solubility of the lithium nitrate increased from about 0.3% (w/v) to some 0.8%. This uncommon phenomenon is most probably connected with the decreasing pH values of the respective initial aqueous solution. On the other hand, an increased amount of nitric acid in experiments 8–14 leads to an increase of the lithium nitrate solubility in the organic layer from 0.1% to about 7%.

Paper-chromatographic experiments

The R_F values obtained for ions which moved on the paper are presented in Table II. In addition to these, potassium and thallium(I) nitrates and rubidium and cesium chlorides showed an R_F value of 0.01 and 0.02 in solvents 13 and 14 respectively. Zero R_F values in all solvents were found for the following ions spotted on paper as:

$Ba(NO_3)_2$	$Cd(NO_3)_2$	$Ce(NO_3)_4$	$PdCl_2$
$Sr(NO_3)_2$	$Pb(NO_3)_2$	$Cr(NO_3)_3$	PtH_2Cl_4
$Ca(NO_3)_2$	$AgNO_3$	$Gd(NO_3)_3$	$RhCl_3$
$Mg(NO_3)_2$	$Al(NO_3)_3$	$La(NO_3)_3$	$RuCl_3$
$Cu(NO_3)_2$	$Fe(NO_3)_3$	$Nd(NO_3)_3$	$TiCl_3$
$Mn(NO_3)_2$	$In(NO_3)_3$	$Sm(NO_3)_3$	VCl_3
$Ni(NO_3)_2$	$Ga(NO_3)_3$	$Pr(NO_3)_3$	
$Zn(NO_3)_2$	$Y(NO_3)_3$	GeF_4	Na_2TeO_3
$Co(NO_3)_2$	$Tl(NO_3)_3$	NbF_5	Na_2WO_4
$Be(NO_3)_2$	$Ce(NO_3)_3$	TaF_5	$(NH_4)_2MoO_4$

As expected, no qualitative difference was observed between a system containing both lithium nitrate and nitric acid, and the system containing only the latter: the same cations moved in both systems, the only exception being the selenite ion, which only moved in the presence of lithium nitrate.

The observations concerning the stability of the MIBK saturated with high concentrations of nitric acid, and its behaviour as a chromatographic eluant presented in a previous paper[1], hold for the present system too.

DISCUSSION

The formation of nitrato-complexes is limited to uranium and elements resembling it, gold, cerium(IV) and thorium standing out in this respect[12]. The presence of high concentrations of nitrate ions, either as nitric acid and/or as other nitrates, promotes the formation of species more soluble in the organic layer. This is achieved through two actions: first, the nitrate promotes the formation of more soluble di- and trinitrato-complexes, and second, the common ion shifts the equilibrium of the dissociation toward the undissociated mono-nitrato-form, soluble in organic solvents. In the case of gold (III), the above-mentioned influence of the nitrates present in the solution need not necessarily prevail. Since gold nitrate cannot be purchased and its preparation is difficult[4], the gold was spotted as $AuCl_3$. The influence of nitrates in this case is not necessarily attributable to the formation of gold nitrato-complexes. Tin, antimony and arsenic, of which neither nitrates nor nitrato-complexes are known,

moved on paper as their chlorides. The changes in the R_F values could be ascribed to the differences of acidity in the eluant.

As pointed out, the same qualitative results were obtained when the nitrate in the initial aqueous phase derived either from nitric acid or from lithium nitrate. Quantitatively, there were differences; different R_F values were obtained for the same cation under different conditions. For comparison, curves of the R_F values for a given ion, obtained in the three following systems:

1. varying amounts of nitric acid (in the absence of lithium nitrate),
2. 1 M nitric acid and varying amounts of lithium nitrate, and
3. 1 M lithium nitrate and varying amounts of nitric acid

were plotted against the total NO_3^- concentration in the corresponding initial aqueous solution. The curves for UO_2, Th, Sb, Sn, Au and Hg are shown in Fig. 1. It appears that at relatively low NO_3^- concentration (up to 2–3 M), the R_F values for a given ion do not differ, or differ only slightly, with the source of the nitrate. At higher NO_3^- concentrations, smaller or larger differences are observed. The highest R_F values are obtained when the nitrate ions are derived from nitric acid; lower values are obtained when the nitric acid is partly replaced by lithium nitrate and the lowest values are observed when the source of the nitrate is almost entirely lithium nitrate, with only 1 M nitric acid. Thorium behaves somewhat differently, and with bivalent tin the sequence is reversed. It is interesting to compare curves 1 and 2 (Fig. 1) for
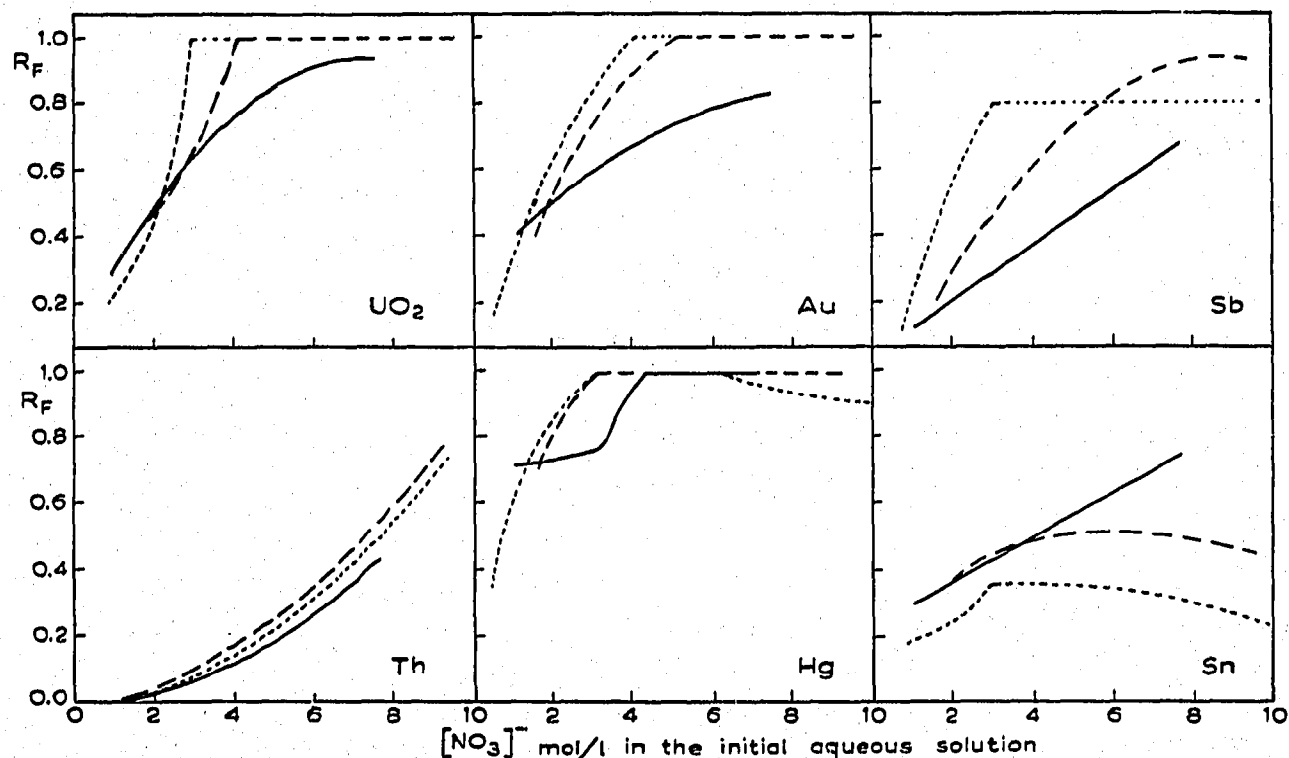

Fig. 1. R_F values of ions plotted against nitrate ion concentration in the initial aqueous solutions. The nitrate ions were derived from: —— varying concentrations of lithium nitrate in the presence of 1 M nitric acid; — — varying concentrations of nitric acid in the presence of 1 M lithium nitrate ; – – varying concentrations of nitric acid only.

the cases of uranyl, mercury and gold. It appears that the $1 M$ lithium nitrate present in the initial aqueous phase has no influence on the R_F values. By deducting nitrate corresponding to a $1 M$ concentration of lithium from curves 2, almost overlapping curves for curves 1 and 2 are obtained. This can be explained on the basis of the results shown in Fig. 2, where the R_F values for the above three ions are plotted
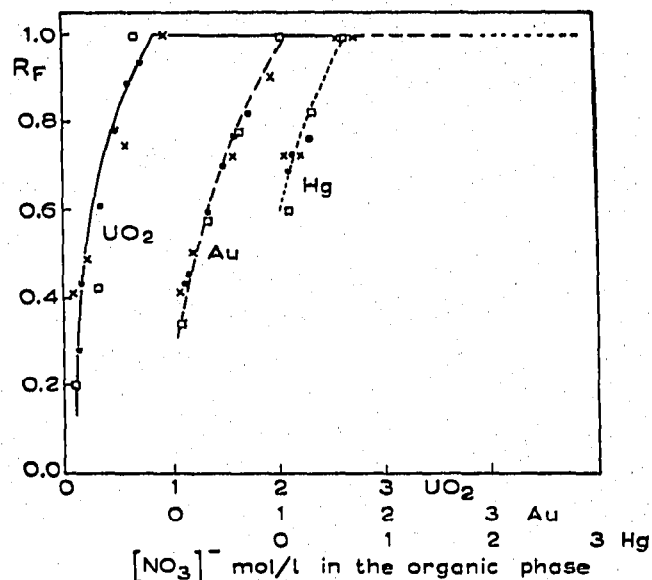
Fig. 2. The R_F values of uranyl, mercury and gold nitrates as a function of nitrate ion concentration in the organic phase. The nitrate ions were derived from: ● varying concentrations of lithium nitrate in the presence of $1 M$ nitric acid; × varying concentrations of nitric acid in the presence of $1 M$ lithium nitrate; □ varying concentrations of nitric acid only.

versus the total NO_3^- concentration in the organic layer only. It can be seen that the R_F values depend roughly upon the total nitrate concentration in the organic layer. Since lithium nitrate is practically absent from the organic phase, its presence in the initial aqueous solution does not influence the R_F values of the above cations.

SUMMARY

The distribution coefficients of nitric acid and lithium nitrate, each in the presence of varying concentrations of the other, between water and methyl isobutyl ketone were determined. The chromatographic behaviour of a number of ions in the above mixtures was studied. It was found that the R_F values of uranyl, thorium and gold nitrates are a function of the nitrate ion concentration in the organic layer.

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