Journal of Chromatography, 135 (1977) 249–255
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CHROM. 9874

Note

The use of aqueous nitrite solutions in reversed-phase chromatography and liquid–liquid extraction

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(Received December 10th, 1976)

Considerable attention has been devoted to reversed-phase chromatography and liquid–liquid extraction in systems involving the use of high-molecular-weight extractants such as long-chain aliphatic amines, substituted quaternary ammonium salts and neutral organophosphorus compounds. Solutions of strong monobasic acids or their alkali metal salts are generally selected as the aqueous phase. Although nitrite ion forms stable complexes with many metal ions, its use in reversed-phase chromatography has not been reported. As for ion-exchange chromatography, Cardaci *et al.*[1] briefly discussed the potentialities of nitrite solutions in the separation of metal ions on a thin layer of a cation- or anion-exchange resin. Bhatnagar and Shukla[2] reported on the use of nitrite solutions in the ion-exchange separation of silver from cobalt and nickel.

This paper describes a study on the use of the substituted quaternary ammonium nitrite–sodium nitrite system in the extraction and chromatography of metal ions.

EXPERIMENTAL

Materials

Aliquat 336 (General Mills, Kankakee, Ill., U.S.A.), a yellow viscous liquid, is a mixture of methyltri-*n*-alkylammonium chlorides with alkyl groups that consist mainly of C_8–C_{10} chains; its mean molecular weight is 475. Conversion into the nitrite salt was effected by two consecutive equilibrations with a concentrated (*e.g.*, 1 *M*) sodium nitrite solution.

In view of the sensitivity to light of the reduction of trivalent to divalent cobalt[3,4], fresh solutions of $Na_3Co(NO_2)_6$ were prepared for each series of experiments on cobalt(III).

In radioactivity experiments, ^{58}Co and ^{115m}Cd (Radiochemical Centre, Amersham, Great Britain) were used as tracers.

All other reagents were of analytical reagent grade.

Chromatography

Thin-layer chromatography was carried out as described in previous papers[5,6], using silica gel (Woelm, Eschwege, G.F.R.) as the support. Suspensions of impregnat-

ed silica gel were prepared by thoroughly mixing 25 g of silica gel with 100 ml of a 0.1 *M* solution of $Aliquat^+NO_2^-$ in chloroform. The solution was stored overnight and agitated again before use. Chromatographic plates were prepared as reported earlier[5,6]. Sample solutions of the ions, containing 1–10 mg/ml of cation [nitrate salts; with Co(III) a $Na_3Co(NO_2)_6$ solution], were applied with the help of a pointed paper wick. Ascending chromatography was carried out for a length of run of 5 or 3 cm (3–5 *M* sodium nitrite), which required about 15 min. After drying the plates in air, detection of all ions was achieved by using a 0.2% solution of 4-(2-pyridylazo)-resorcinol (PAR) in acetone–ethanol (1:1, v/v) and subsequent treatment with ammonia vapour.

Extraction

An aqueous solution of the desired composition was shaken for 3 min with an equal volume of a solution of $Aliquat^+NO_2^-$ in toluene; phase separation was effected by centrifugation. For all metal ions except silver, the metal content of an aliquot of the aqueous phase, both before and after extraction, was determined by atomic-absorption spectrometry with electrothermal atomization. If the percentage extraction was low, the organic phase was back-extracted three times with 0.25 *N* nitric acid, and the re-extract analyzed. Silver was determined by diluting 5 or 10 ml of the organic extract with 70 ml of ethanol and subsequent titration with a standardized potassium iodide solution.

With cobalt(II), cobalt(III) and cadmium(II), extraction experiments were also performed using radioactive solutions. To an inactive solution, enough ^{58}Co or ^{115m}Cd was added to give 1500–2000 counts/min per millilitre of solution (integral counting; with a background of *ca.* 20 counts/min). After extraction and separation of the phases, 5-ml portions were counted for γ-activity. The organic cobalt-containing extracts were also analyzed by UV–visible spectrometry.

Apparatus

A Perkin-Elmer Model 403 atomic-absorption spectrophotometer equipped with an HGA 72 graphite cell was used for atomic-absorption analysis, and an LKB-Wallac 1280 Ultrogramma with a 3-in. NaI(Tl) crystal was used to count the γ-activities. The UV–visible spectra were recorded on a Beckman Acta CIII spectrophotometer.

RESULTS AND DISCUSSION

Chromatography

Reversed-phase chromatography in the Aliquat-impregnated silica gel–aqueous sodium nitrite solution system was carried out for nine ions, using 0–5 *M* sodium nitrite solution as the mobile phase. The results are presented in Fig. 1. In experiments on non-impregnated silica gel, for all ions except zinc(II), R_F values of 0.9–1.0 were consistently found at aqueous nitrite concentrations above 0.1 *M*; streaking was observed at lower concentrations. The graph of R_F *versus* NO_2^- molarity for zinc(II) on plain silica gel is included in Fig. 1 (dotted line).

With both di- and trivalent cobalt, streaking and/or formation of double spots was repeatedly observed. As discussed in more detail below, this effect is due to the

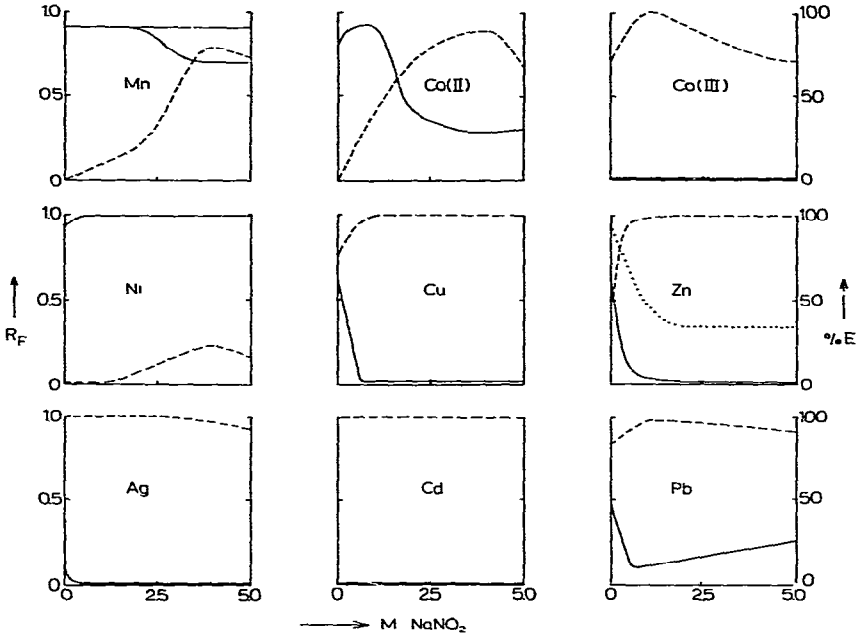

Fig. 1. Graphs of R_F *versus* concentration of sodium nitrite solution for nine ions obtained in chromatography with silica gel impregnated with Aliquat$^+NO_2^-$ (solid lines) or non-impregnated silica gel (dotted line) as the stationary phase. The broken lines represent percentage extraction *versus* concentration of sodium nitrite solution in the system $5 \cdot 10^{-3}$ *M* metal ion in *x M* sodium nitrite solution–0.1 *M* Aliquat$^+NO_2^-$ in toluene.

oxidation of cobalt(II) at high and the reduction of cobalt(III) at low nitrite concentrations. No explanation can as yet be given for the occurrence of dumb-bell-shaped spots for manganese(II) at high nitrite concentrations. The sorption of silver(I) and lead(II) is not due to precipitation of the metal ions as their chloride salts, as sorption is negligible on non-impregnated silica gel. The high percentages of extraction observed for these ions in liquid–liquid extraction (see below) support the suggestion that sorption is due to the formation of anionic nitrito complexes.

It is also interesting to note that our results show good agreement with those published by Cardaci *et al.*[1] for the Ionex-25 SB-Ac–1 *M* sodium nitrite solution system, as illustrated by the R_F values in Table I.

Liquid–liquid extraction

Results for the extraction of the nine ions under discussion by a 0.1 *M* solution of Aliquat$^+NO_2^-$ in toluene are included in Fig. 1. Obviously, the extraction efficiency varies in the same order as the sorption strength in reversed-phase chromatography. This result is according to expectations, based on the relationship

$$D = k\,(1/R_F - 1) \qquad (1)$$

where D is the distribution coefficient of the metal ion in liquid–liquid extraction and k is a constant, which has been verified for, *e.g.*, chloride, bromide and nitrate systems[7].

TABLE I

COMPARISON OF R_F VALUES OBTAINED WITH TWO DIFFERENT STATIONARY PHASES USING 1 *M* SODIUM NITRITE SOLUTION AS ELUENT

Ion	*Stationary phase*	
	Silica gel impregnated with Aliquat$^+NO_2^-$	*Polygram Ionex-25 SB-Ac**
Mn(II)	0.90	0.95
Co(III)	0.00	0.00
Ni(II)	1.00	0.90
Cu(II)	0.00	0.10
Zn(II)	0.05	0.05
Ag(I)	0.00	0.00
Cd(II)	0.00	0.00
Pb(II)	0.10	0.10

* Strongly basic ion-exchange thin layer in the acetate form.

From the results in Fig. 1, a number of interesting separations can be postulated. Fox example, nickel(II) can be separated from ions such as cadmium(II), zinc(II), copper(II) and silver(I) using 1 *M* sodium nitrite solution. An effective separation of cadmium(II) from cobalt(II) and manganese(II) can be achieved when using an aqueous phase to which no sodium nitrite has been added. As an example, sample solutions containing $5 \cdot 10^{-5}$–$5 \cdot 10^{-3}$ *M* of cadmium(II) and cobalt(II) as their nitrate salts were treated with an equal volume of 0.1 *M* Aliquat$^+NO_2^-$ in toluene. In all experiments, percentage extraction of cadmium was over 99.5%, while that of cobalt was less than 0.1%.

Nature of metal–nitrito complexes

Four ions, *viz.*, cobalt(II), cobalt(III), silver(I) and cadmium(II), were selected to study the nature of the extracted metal–nitrito complex anions. With silver and cadmium, maximum loadings of a 0.03 *M* solution of Aliquat$^+NO_2^-$ in toluene for the former ion and a 0.1 *M* solution for the latter were determined, using 6.0 or 2.5 *M* sodium nitrite solution, respectively, as the aqueous phase. The ratios $[Ag(I)/Aliquat]_{org.}$ and $[Cd(II)/Aliquat]_{org.}$ had limiting values of 1.0 and 0.5, respectively, *i.e.*, extraction occurs according to the equations

$$R_4N^+NO_2^-{}_{org.} + Ag(NO_2)_2^- \rightleftharpoons R_4N^+Ag(NO_2)_2^-{}_{org.} + NO_2^- \quad (2)$$

and

$$2\ R_4N^+NO_2^-{}_{org.} + Cd(NO_2)_4^{2-} \rightleftharpoons (R_4N^+)_2Cd(NO_2)_4^{2-}{}_{org.} + 2\ NO_2^- \quad (3)$$

The formation of $Ag(NO_2)_2^-$ was suggested earlier by Bhatnagar and Shukla[2].

Studies on the mechanism of extraction of cobalt(II) and cobalt(III) in systems involving the use of nitrite solutions are seriously hindered by the fact that, especially in acidic solutions, the former ion is easily oxidized to the latter:

$$4\ Co(H_2O)_6^{2+} + 24\ NO_2^- + 4\ H^+ + O_2 \rightleftharpoons 4\ Co(NO_2)_6^{3-} + 26\ H_2O \quad (4)$$

On the other hand, as can be seen from the same equation, in the absence of a sufficient excess of nitrite ions cobalt(III) will be easily reduced to cobalt(II). In the present work, such redox phenomena must be absent and a preliminary study was therefore carried out in order to select favourable experimental conditions. Absorption spectrometry at 460 nm [$\varepsilon_{Co(III)} \gg \varepsilon_{Co(II)}$ for nitrite solutions] and liquid–liquid extraction [$D_{Co(III)} > D_{Co(II)}$ at low NO_2^- concentrations, *cf.*, Fig. 1] with subsequent radiochemical analysis were used as methods of analysis. From several series of experiments, it was concluded (1) that for concentrations of sodium nitrite solution up to 2.5 *M*, the percentage oxidation of cobalt(II) in solutions containing 0.005–0.5 *M* cobalt(II) is negligible over a period of at least 30 min, provided that no free acid is present in the solution; and (2) that even with neutral solutions and prolonged periods of time (several hours), reduction of cobalt(III) need not be considered if the aqueous solution has a nitrite concentration of *ca.* 1 *M* or higher.

Three methods of analysis were used to assess the composition of the cobalt(II)-containing complex present in the organic phase. As shown in Fig. 2a, a plot of log $D_{Co(II)}$ *versus* log[Aliquat$^+$NO$_2^-$] has a slope of 1.0. On the other hand, the method of continuous variation (Fig. 2b) and a maximum loading of a 0.1 *M* solution of Aliquat in toluene with cobalt(II) (Fig. 2c) both indicate that the ratio [Co(II)/Aliquat]$_{complex}$ is 0.5. Admittedly, in the maximum-loading experiments, a fairly high nitrite concentration (2.5 *M*) had to be used in order to achieve a sufficiently high level of extraction. As a consequence, some conversion of cobalt(II) into cobalt(III) and subsequent extraction of cobalt(III) cannot be wholly excluded; possibly this would explain the unusually large scatter of the results obtained at high cobalt(II) concentrations. However, it seems justified to conclude that at relatively high aqueous cobalt(II) concentrations extraction proceeds according to the equation

$$2\ R_4N^+NO_2^-{}_{org.} + Co(NO_2)_4^{2-} \rightleftharpoons (R_4N^+)_2Co(NO_2)_4^{2-}{}_{org.} + 2\ NO_2^- \qquad (5)$$

As for the results obtained at low cobalt(II) concentrations, the log–log plot suggests the presence of $Co(NO_2)_3^-$ in the organic phase. However, the UV–visible

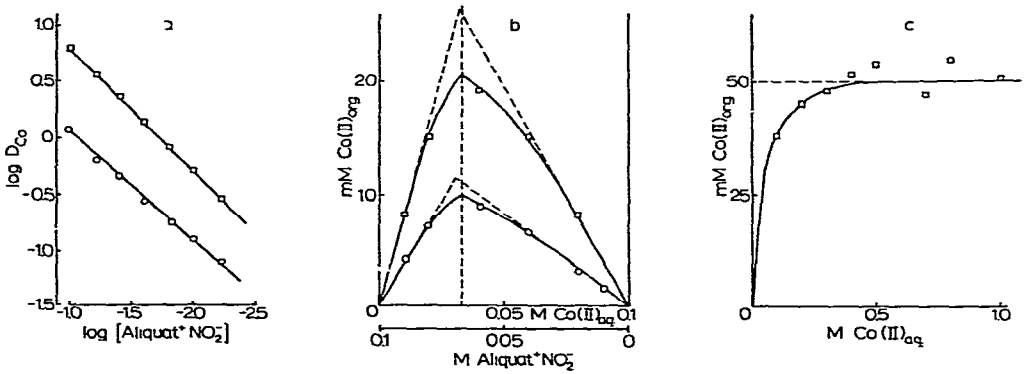

Fig. 2. Elucidation of the nature of the cobalt(II)-containing complex by different methods of analysis. (a) Log $D_{Co(II)}$ *versus* log [Aliquat$^+$NO$_2^-$]. Aqueous phase, $5 \cdot 10^{-3}$ *M* Co(II) in 1.0 *M* (○) and 2.5 *M* (□) sodium nitrite solution. (b) Job curve for the system *x M* Aliquat$^+$NO$_2^-$ in toluene–($10^{-1}-x$) *M* cobalt(II) in 1.0 *M* (○) and 2.5 *M* (□) sodium nitrite solution. (c) Maximum loading of 0.1 *M* Aliquat$^+$NO$_2^-$ in toluene. Aqueous phase, 0–1 *M* cobalt(II) in 2.5 *M* sodium nitrite solution. Extraction of cobalt(II) by toluene itself is negligible.

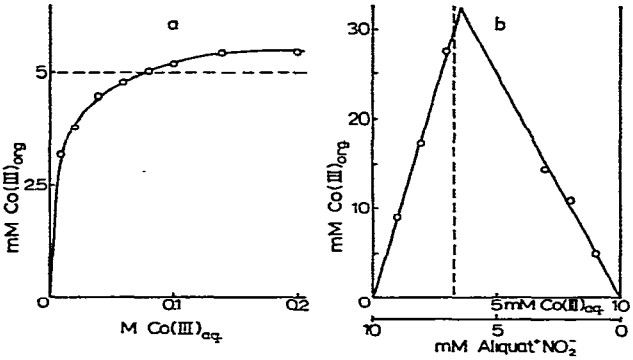

Fig. 3. Elucidation of the nature of the cobalt(III)-containing complex by different methods of analysis. (a) Maximum loading of 0.01 *M* Aliquat$^+$NO$_2^-$ in toluene. Aqueous phase, 0–0.2 *M* cobalt(III) in 2.5 *M* sodium nitrite solution. (b) Job curve for the system *x M* Aliquat$^+$NO$_2^-$ in toluene–(10^{-2} – *x*) *M* cobalt(III) in 2.5 *M* sodium nitrite solution. Extraction of cobalt(III) by toluene itself is negligible.

spectra of organic extracts of aqueous solutions containing 0.005 and 0.1 *M* cobalt(II) are identical, displaying maximum absorption at 550 nm, log ε being calculated as 2.15 in both instances*. The latter result strongly suggests that a single complex anion, *i.e.*, $Co(NO_2)_4^{2-}$, is present in the organic phase, irrespective of the aqueous metal ion concentration; that is, the slopes of the curves in Fig. 2a must be ascribed to the well known irregular behaviour of log–log plots.

With cobalt(III), both a maximum loading of 0.01 *M* Aliquat dissolved in toluene (Fig. 3a) and the method of continuous variation (Fig. 3b) indicate that the ratio $[Co(III)/Aliquat]_{complex}$ is 0.5, *i.e.*, the overall composition of the extracted complex is $Co(NO_2)_3 \cdot 2Aliquat^+NO_2^-$ and the metal-containing species is probably $Co(NO_2)_5(H_2O)^{2-}$. Extraction can be described by the equation

$$2\,R_4N^+NO_2^-{}_{org.} + Co(NO_2)_5(H_2O)^{2-} \rightleftharpoons (R_4N^+)_2Co(NO_2)_5(H_2O)^{2-}{}_{org.} + 2\,NO_2^- \quad (6)$$

Unfortunately, the presence of a (single) molecule of water in the extracted complex cannot be demonstrated, as it is impossible to carry out Karl Fischer titrations in nitrite solutions.

It is interesting to note that Carunchio and Ara Gerardi[9] isolated fractions containing $Co(NO_2)_3(H_2O)_3$, $Co(NO_2)_4(H_2O)_2^-$ and $Co(NO_2)_6^{3-}$ by means of ion-exchange chromatography on a DEAE-cellulose column. The decomposition of hexanitritocobaltate(III) (sodium salt; pH = 5.2–6.5; open vessel) was found to take a considerable time, significant changes occurring only after several days.

The fraction containing $Co(NO_2)_6^{3-}$ displays maximum absorption at *ca.* 360 nm, and the value of log ε is 3.9. Surprisingly, the values of $\lambda_{max.}$ and log $\varepsilon_{max.}$ for the cobalt(III)-containing species present in our organic extracts are 363 nm and

* Goodgame and Hitchman[8] reported $\lambda_{max.}$ = 526 nm (log ε = 2.02) for [*o*-xylylenebis(triphenylphosphonium)]$Co(NO_2)_4$ dissolved in acetonitrile. In the present study, $\lambda_{max.}$ = 525 nm was observed on mixing solutions of Aliquat$^+$NO$_2^-$ and $Co(NO_2)_2$ in ethanol.

3.9, respectively, that is, they are virtually identical with those reported by Carunchio and Ara Gerardi[9] and also by Von Kiss and Von Czeglédy[10], for $Co(NO_2)_6^{3-}$. On the other hand, other workers at this University[11] observed that the substitution of nitrite ligands by water molecules in $Co(NO_2)_{6-n}(H_2O)_n^{(n-3)+}$ complexes occurs so fast that isolation of the individual complexes is impossible. Analysis of data obtained in kinetic experiments has permitted the unequivocal identification of a single species only, *viz.*, $Co(NO_2)_5(H_2O)^{2-}$. In accord with this result, Matsko *et al.*[12], in a study on the isotopic exchange of a nitrite ion in sodium hexanitritocobaltate(III), also postulated pentanitritocobaltate(III) as an intermediate. Obviously, further work will be necessary before a definite conclusion concerning the nature of cobalt(III)-containing species present in and/or extracted from aqueous nitrite solutions can be drawn.

ACKNOWLEDGEMENTS

The radiochemical analyses were performed in the Radionuclide Centre of the Free Reformed University. Thanks are due to Dr. M. W. G. de Bolster for stimulating discussions during the preparation of the manuscript.

REFERENCES

1 V. Cardaci, M. Lederer and L. Ossicini, *J. Chromatogr.*, 101 (1974) 411.
2 R. P. Bhatnagar and R. P. Shukla, *Anal. Chem.*, 32 (1960) 777.
3 A. K. Bhattacharya and N. R. Dhar, *Z. Anorg. Allg. Chem.*, 175 (1928) 357.
4 A. K. Bhattacharya and N. R. Dhar, *Z. Anorg. Allg. Chem.*, 176 (1928) 372.
5 G. de Vries and U. A. Th. Brinkman, *J. Chromatogr.*, 64 (1972) 374.
6 U. A. Th. Brinkman, G. de Vries, R. Jochemsen and G. J. de Jong, *J. Chromatogr.*, 102 (1974) 309.
7 U. A. Th. Brinkman, *Progr. Separ. Purif.*, 4 (1971) 241.
8 D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc., A*, (1967) 612.
9 V. Carunchio and M. Ara Gerardi, *J. Chromatogr.*, 31 (1967) 653.
10 A. von Kiss and D. von Czeglédy, *Z. Anorg. Allg. Chem.*, 235 (1938) 407.
11 J. Breman and C. Dekker, unpublished results.
12 I. V. Matsko, Yu. E. Selyaninov and G. A. Shagisultanova, *Russ. J. Inorg. Chem.*, 12 (1967) 351.