CHROMATOGRAPHY OF ANIONS ON SILICA GEL THIN LAYER

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The paper gives results of investigation of behaviour of the anions PO_4^{3-}, MoO_4^{2-}, TcO_4^-, RuO_4^{2-}, TeO_3^{2-} and (in part) I^- during thin-layer chromatography with silica gel adsorbent and mixtures of alcohols with aqueous ammonia as eluent systems. For migrating anions the R_F changes due to changes of the organic to aqueous phase ratio, analytical concentration of ammonium ions, the alcohol used in the eluent system, and concentration of the anions in solutions of samples have been determined. Correlation between R_F of the anions and dielectric constant of the eluent systems have been followed; relation between the both variables can be expressed by approximative equation $R_F = k \log \varepsilon + \log q$.

There are not too many data in literature concerning behaviour of inorganic anions during thin-layer chromatography. Early papers deal with separation of halogenides, phosphates, sulphates, and polythionates[1,2], effect of cations on their separation being studied with the use of special chromatographic layers with added cation exchange resin[3]. Recently TLC separation of anions became important due mainly to its use as checking, detection and separation method for radioactive iodine compounds; it is used by both manufacturers and users for purity determination of commercial and laboratory prepared inorganic and organic radioiodine compounds[4-9], separation of its various chemical forms[10,11], or as a detection method[12]. TLC is reported, too, to be used for separation and purification of other radionuclides existing in anionic form *e.g.* in mixtures of fission products of uranium[13].

Behaviour of anions during thin-layer chromatography is markedly affected by chosen experimental conditions, especially by the adsorbent used in the chromatographic layer and composition of the used eluent system. Behaviour of iodide, iodate and periodate in silica gel chromatographic layers was studied[11] by means of the radioisotope using eluent mixtures of aqueous ammonia with C_1 to C_5 saturated open-chain alcohols.

The present paper summarizes results of analogous study especially for those anions for which ref.[13] gives certain data about their behaviour during TLC with alumina as adsorbent and plaster as binder.

EXPERIMENTAL

All the chemicals and solvents used were *p.a.* purity grade. Concentrations of stock solutions were checked analytically, and the organic solvents were distilled. Commercial TLC plates Silufol (Kavalier Glass Works, ČSSR) were used (wide-porous silica gel with starch binder on aluminium plates). The radioisotopes ^{32}P, ^{99}Tc, and ^{131}I were used in the commercial produced forms: $Na_2H^{32}PO_4$ (Zentralinstitut für Kernforschung, Dresden, GDR) containing more than 98% carrier-free $^{32}PO_4^{3-}$ with the volume activity 0·7 GBq . ml^{-1} in solutions with concentrations 9·1 mg NaCl and 0·6 mg $NaHCO_3$ per 1 ml; $NH_4{}^{99}TcO_4$ in 0·1M-NH_4OH (The Radiochemical Centre, Amersham, GB) with volume activity 16 MBq . ml^{-1}; the used solution of $K^{131}I$ (USSR) with volume activity 210 MBq . ml^{-1} was also carrier-free, and, according to our check, it did not contain any other chromatographically detectable chemical forms of radioiodine. Potassium ruthenate ($K_2{}^{106}RuO_4$) was prepared in laboratory: solution of ^{106}Ru chlorocomplexes in 4M-HCl (The Radiochemical Centre, Amersham, GB) with volume activity 37 MBq . . ml^{-1} was oxidized with potassium permanganate in diluted (1 : 1) sulphuric acid without addition of carrier to give gaseous $^{106}RuO_4$ (ref.[14]); this gas was expelled from the solution with air flow and trapped in 1M-KOH. Volume activity of the obtained $K_2{}^{106}RuO_4$ was not determined, it was, however, relatively low. Potassium molybdate ($K_2{}^{99}MoO_4$) was obtained by dissolving 60 mg MoO_3 (irradiated with the neutron flux density $2 . 10^{17}$ m^{-2} s^{-1} in a reactor VVR-S for two weeks) in 2·5 ml solution 1M-KOH + 2·5M-K_2CO_3 (1 : 5); the molybdate solution obtained was 0·25M, and its volume activity was 20 MBq . ml^{-1} when used. The carrier preparations were prepared by addition of radioactive tracer to solutions of the same salt of various molarities, only in the case of molybdate the solutions were obtained by dilution of the stock solution. Solution of K_2TeO_3 was prepared by dissolution of TeO_2 in 1M-KOH.

Two chromatograms 25 × 150 mm were developed at once in a chromatographic box with ascending arrangement, the slope of the plates being $\alpha = 0·6$ rad. The chromatograms were developed immediately after spotting and drying of the solution of the anion studied, 50 ml eluent mixture alcohol–aqueous ammonia being used in each case. The individual eluent systems differed in the alcohol used, the ratio of organic and aqueous phase φ ($= V_0/V_w$), and overall analytic concentration of ammonium ions $c_{NH_4^+}$. Position of spots of the individual compounds in the dried chromatogram was determined radiometrically (^{32}P, ^{99}Mo, ^{99}Tc and ^{131}I) using a window-type G-M counter, or autoradiographically (^{106}Ru) using a X-ray film Strukturix FW-D4P (Agfa-Gevaert, Belgium). Detection of TeO_3^{2-} was carried out by spraying the chromatogram with 5% $SnCl_2$ solution, the compound spot appearing as black colouration of the reduced tellurium metal.

RESULTS AND DISCUSSION

Volume ratio change of organic and aqueous phases in the eluent system has a marked influence on behaviour of the studied anions in chromatographic layers when using any of the unibasic alcohols derived from saturated non-cyclic hydrocarbons, as it was the case with I^- and IO_3^-, too[11]; with respect to the miscibility of the alcohols with water it is possible to use the C_1 to C_5 alcohols only. The only exceptions are RuO_4^{2-} and TeO_3^{2-} which remain at the start line in all the cases as it was the case with IO_4^-, too. This behaviour of RuO_4^{2-} was also observed in TLC with alumina and NH_4OH–water eluent[13], and it was explained by reduction of RuO_4^{2-} to ruthenium dioxide.

Effect of φ on migration of the anions for the first three saturated alcohols and constant concentration of ammonium ions in the eluent system ($c_{NH_4^+} = 0·5$ mol . l^{-1}) is given in Figs. 1 and 2. Relation between R_F values and volume ratio of organic to aqueous phase in the eluent system is given in Fig. 1 for TcO_4^- and MoO_4^{2-} and in Fig. 2 for PO_4^{3-} and RuO_4^{2-}. All the dependences were obtained and are valid for analytical concentrations of the anions in solutions lower than 10^{-3} mol . l^{-1}. From the results it follows that mobilities of PO_4^{3-} and MoO_4^{2-} are much more sensitive to change in φ than that of TcO_4^-, and, furthermore, it is observed that lowering of the anion migration is greater when replacing methanol by ethanol than that caused by replacing ethanol by propanol.

The alcohol-free eluent system NH_4OH–water is not as efficient in separation o anions on silica gel chromatographic layers as it is reported[13] to be on alumina layers. All our results of elution with 0·5M aqueous ammonia (curves for $\varphi = 0$ in Figs 1 and 2) as well as with other analytical concentrations show only two extreme cases: the anions either move with the solvent front (TcO_4^-, MoO_4^{2-}, PO_4^{3-}, I^-, IO_3^-) or remain at the start line (RuO_4^{2-}, TeO_3^{2-}, IO_4^-).

The analytical concentration of ammonium ions in eluent system does not affect mobilities of the individual ions to such an extent as changes in volume ratios of organic to water phase, nevertheless its influence is not negligible (Fig. 3). The change of $c_{NH_4^+}$ in the system has the smallest and the greatest effect on the mobilities of TcO_4^- and MoO_4^{2-}, respectively. The course of curve *2* in Fig. 3 is, however, a result of two phenomena *viz.* effect of concentration of ammonium ions in the eluent mixture and effect of concentration of the MoO_4^{2-} solution spotted on the chromatogram. The dependences R_F–$c_{NH_4^+}$ for a given system alcohol–aqueous ammonia

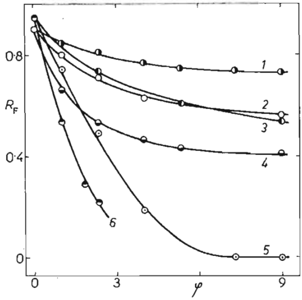

FIG. 1

Change of R_F of TcO_4^- and MoO_4^{2-} with Ratio of Volumes of Organic and Aqueous Phases (φ) in Eluent Mixture with $c_{NH_4^+} = 0·5M$

1 TcO_4^-, methanol; *2* TcO_4^-, ethanol; *3* MoO_4^{2-}, methanol; *4* TcO_4^-, 1-propanol; *5* MoO_4^{2-}, ethanol; *6* MoO_4^{2-}, 1-propanol.

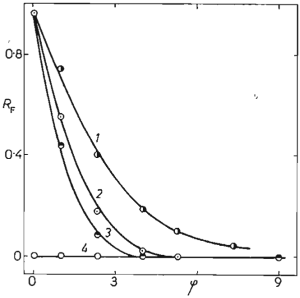

FIG. 2

Dependence of R_F of Phosphate and Ruthenate(IV) on Ratio of Volumes of Organic and Aqueous Phases (φ) in Eluent Mixture with $c_{NH_4^+} = 0·5M$

1 PO_4^{3-}, methanol; *2* PO_4^{3-}, ethanol; *3* PO_4^{3-}, 1-propanol; *4* RuO_4^{2-}, all alcohols.

differ somewhat in the slope values for various anions, but a mild influence can be observed also for any anion when changing alcohol component or the value φ of the mixture. From practical point of view, however, it is important that influence of $c_{NH_4^+}$ is not so fundamental as that of the factor φ.

The effect of alcohols on R_F values of the individual anions was studied at constant value $c_{NH_4^+} = 0{\cdot}5 \text{ mol} . \text{l}^{-1}$ and at various ratios φ. Concentrations of the solutions of anions spotted on the chromatogram were below 10^{-3}M. Fig. 4 shows the dependence of R_F on the number of carbon atoms n in the molecule of the alcohol used, mobility of all the migrating anions being decreased with increasing n. Value of the ratio φ affects character of this dependence. For low value φ course of the dependence is convex to x-axis (which is clearest within $n = 1$ to 3), and it changes to concave course at sufficiently high φ values. The curves show that this is general for all the migrating anions; the same behaviour was found by us earlier for IO_3^-, too. Experimental study of this phenomenon is limited due to considerable decrease in miscibility of water and alcohol with its increasing n: the available values are $\varphi \geqq 6$ and $\varphi \geqq 9$ for butanol and pentanol, respectively.

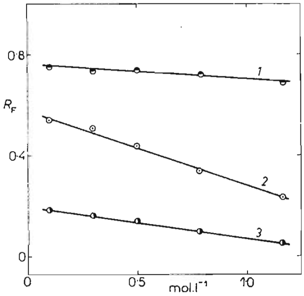

FIG. 3

Influence of Ammonium Ion Concentration ($c_{NH_4^+}$) in Mixtures NH_4OH–Ethanol at $\varphi = 2{\cdot}3$

1 TcO_4^-, carrier-free; *2* MoO_4^{2-}, 0·25M solution; *3* PO_4^{3-}, carrier-free.

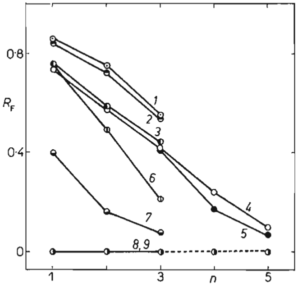

FIG. 4

Influence of Alcohol on R_F Values of the Anions; n Number of Carbon Atoms in the Alcohol; $c_{NH_4^+} = 0{\cdot}5$M

1 MoO_4^{2-}, normal alcohols, $\varphi = 1$; *2* TcO_4^-, normal alcohols, $\varphi = 2{\cdot}3$; *3* PO_4^{3-}, normal alcohols, $\varphi = 1$; *4* TcO_4^-, normal alcohols, $\varphi = 9$; *5* TcO_4^-, isoalcohols, $\varphi = 9$; *6* MoO_4^-, normal alcohols, $\varphi = 2{\cdot}3$; *7* PO_4^{3-}, normal alcohols, $\varphi = 2{\cdot}3$; *8* RuO_4^{2-}, all alcohols and all φ; *9* TeO_3^{2-}, all alcohols and all φ.

Behaviour of TcO_4^- was studied within the whole practically useful range of n, mobility decrease of the other studied anions being so steep with increasing φ value that the $R_F = 0$ value is reached as soon as with ethanol: MoO_4^{2-} for $\varphi > 6{\cdot}5$, PO_4^{3-} for $\varphi > 4{\cdot}5$. Branched-chain alcohols slow down somewhat the migration of TcO_4^- in chromatographic thin layers with silica gel adsorbent as compared with the straight-chain alcohols; the same effect was observed[11] for I^-.

As dielectric constants ε of straight-chain alcohols are inversely proportional to their number of carbon atoms (n), it was stated[11] that decrease of R_F value with increasing **n** implicates a correlation between mobility of a certain anion in chromatographic layer and the value of dielectric constant of the used alcohol–ammonia eluent mixture. Recently it was possible to obtain sufficient amount of data from experimental measurements of physical quantities in mixtures of organic solvents and water[15] wherefrom dielectric constants were determined for most eluent systems used by us. Fig. 5 gives a graphical representation of correlation between R_F and ε for TcO_4^- and I^- with the use of eluent systems containing straight-chain alcohols. In both the cases the correlation is positive, qualitatively identical, but imperfect. Position of the experimental points indicates certain groupings of R_F values into series

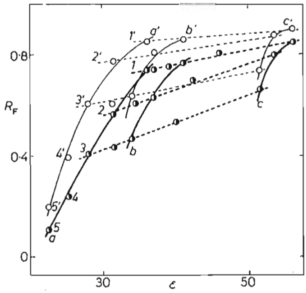

FIG. 5

Correlation between R_F Values of TcO_4^- and I^- and Dielectric Constants ε of Eluent Alcohol–Ammonia Mixtures

TcO_4^- ◑, the curves denoted with simple symbols; I^- ○, the curves denoted with dashed numbers and letters.

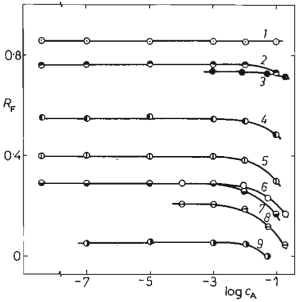

FIG. 6

Influence of Anion Concentration on R_F Values at $c_{NH_4^+} = 0{\cdot}5M$

1 I^-, ethanol, $\varphi = 2{\cdot}3$; *2* PO_4^{3-}, methanol, $\varphi = 1$; *3* MoO_4^{2-}, methanol, $\varphi = 2{\cdot}3$; *4* PO_4^{3-}, ethanol, $\varphi = 1$; *5* PO_4^{3-}, methanol, $\varphi = 2{\cdot}3$; *6* MoO_4^{2-}, 1-propanol, $\varphi = 1{\cdot}9$; *7* I^-, 2-methyl-1-propanol, $\varphi = 9$; *8* MoO_4^{2-}, 1-propanol, $\varphi = 2{\cdot}3$; *9* PO_4^{3-}, ethanol, $\varphi = 2{\cdot}3$.

for individual alcohols (in Fig. 5 denoted by numerical indexes) and for the chosen φ values (denoted by letters). The R_F values of TcO_4^- and I^- belonging to eluents with the individual alcohols could even be connected by straight lines in Fig. 5. However, processing of the data for the other anions showed that this relation is not general. Thus in mixtures methanol–ammonia the linear course is not observed with MoO_4^{2-}, and in the ethanol–ammonia mixtures greater part of the anions studied deviate (MoO_4^{2-} and IO_3^- markedly, TcO_4^- and I^- perceptibly).

Mathematical processing of all the data obtained by us indicates that there is an oblique correlation between the R_F values of the anions and ε values of alcohol–ammonia eluent mixtures which can be expressed by general function $R_F = k \,.\, \log \varepsilon + \log q$, the constants k, q being characteristical for the migiating anion.

The TLC analysis of MoO_4^{2-} gave various R_F values depending on whether the starting (0·25M) or diluted ($<10^{-3}$M) solution of K_2MoO_4 was spotted on the thin layer. Similar phenomenon is mentioned in literature for IO_3^-, too, the observed change being either an increase[10] or decrease[16] of R_F value above a certain limit of IO_3^- concentration. Trying to decide what is the character of the concentration dependence of the anion solution and whether this phenomenon is due to the adsorbent exchange capacity being surpassed or depends on the anion studied (the R_F change with concentration was observed[16] with IO_3^- but not with I^-), we carried out several series of experiments with solutions of MoO_4^{2-}, PO_4^{3-} and I^- of various concentrations ranging from the carrier-free ($<10^{-9}$M) to approximately 10^{-1}M solution. For evaluation of possible influence of the used alcohol and ratio of organic to aqueous phase in the mixture on this phenomenon the chromatograms were developed in various systems chosen in such a way that the final effect could be evaluated for each anion at various velocities of its migration. Effect of the anion concentration in TLC with silica gel adsorbent is seen from Fig. 6. Course of the dependences allows to draw some general conclusions. The concentration effect is felt markedly as far as at the anion concentrations above 10^{-3}M. In all the cases the R_F values decrease with increasing amount of the migrating anion, which is specific property of chromatographic layers with silica gel adsorbent (the reported increase of R_F values for increasing IO_3^- concentrations[10] concerns alumina layers). The faster the anion migrates in the layer, the smaller is the influence of its concentration, and if the solvent front is followed, then the R_F value decrease is not observed or is small or negligible. Furthermore, with increasing mobility of the anion also the lower concentration limit increases from which the effect starts to make itself felt. At low mobilities the effect of the anion concentration is large and influences markedly the applicability of TLC method for separation purposes, if more concentrated solutions have to be used. Spots of the chromatographed compounds become blurred and partially overlapped. The concentration effect is a general phenomenon in TLC, and it depends only on the conditions of elution of the chromatogram, whether and to what extent it will make itself felt with the particular anion. This conclusion is confirmed by courses of the curves of I^- (Fig. 6, curves *1* and *7*).

Choice of the alcohol and ratio of organic to aqueous phase makes it possible to prepare eluent systems allowing to use chromatographic thin layer with silica gel adsorbent for solution of various problems, be it for determination and separation of the individual anions or their purification in alkaline solutions. Of course, composition of the eluent solution will make itself felt also in another important chromatographical criterion, *i.e.* time of elution of the chromatogram. This fact followed from investigation of velocities of advance of alcohol–water solutions along the chromatographic layer[11]. At present the results of the systematic study carried out are practically used *e.g.* in preparation of pure samples of ^{99}Mo, in studies of chemical forms of radioiodine in the generators ^{99}Mo – ^{99}Tc, and in checking chemical and radiochemical purity of commercial samples of radioiodine.

REFERENCES

1. Seiler H., Erlenmeyer H.: Helv. Chim. Acta *47*, 264 (1964).
2. Achrem A. A., Kuznecova A. I.: *Tonkosloynaya Chromatografia*, p. 155. Izd. Nauka, Moscow 1964.
3. Brezgunova I. N., Smolyaninov V. V., Kharlamova N. I.: Zh. Fiz. Khim. *45*, 1785 (1971).
4. de Salas G. N. B., Alvarez J., Mitta A. E. A.: Radiochim. Acta *17*, 58 (1972).
5. Maděra V., Matucha M., Novák J.: Radioizotopy *12*, 707 (1971).
6. Melo S. C., Podlech P. S., Barberio J. C.: Report IEA-204/1969.
7. Tanase M., Shikata E., Amano H.: J. Nucl. Sci. Technol. (Tokyo) *13*, 125 (1976).
8. Zelenay K., Nowak K., Pasternak A.: Nukleonika *18*, 417 (1973).
9. Beneš J., Konůpek M.: Jad. Energ. *22*, 144 (1976).
10. Maki Y.: J. Radioanal. Chem. *27*, 33 (1975).
11. Beneš J.: This Journal, in press.
12. Mráz L., Stollarová N., Palágyi Š.: Isotopenpraxis *11*, 66 (1975).
13. Maki Y., Murakami Y.: Nippon Kagaku Kaishi *1973*, n°. 1,85.
14. Kepák F., Uher E., Pecák V.: Research Report UJV Řež 4100/Ch/1977.
15. Velich V.: Private communication.
16. Palágyi Š., Zaduban M.: Chem. Zvesti *23*, 876 (1969).

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