

## BEHAVIOUR OF IODIDE, IODATE AND PERIODATE IN TLC WITH ALCOHOL-AQUEOUS AMMONIA ELUENT

Jaroslav BENEŠ

*Institute of Radiation Dosimetry,  
Czechoslovak Academy of Sciences, 180 86 Prague 8*

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The behaviour of  $I^-$ ,  $IO_3^-$  and  $IO_4^-$  in silica gel thin layer chromatography and their separation with ammonia-alcohol eluents (saturated open-chain C1 to C5 alcohols being used) have been studied with the help of radioisotopes. Changes in  $R_F$  values of the studied anions caused by changes of the alcohol, ratio of the organic to aqueous phase in the mixture, and overall analytical concentration of ammonium ions have been determined. Influence of alcohol on kinetics of development of the chromatograms with the alcohol-water mixtures has been determined, too.

The eluent systems used for chromatographic separation of halogenides and various iodine compounds on thin layers or paper contain ammonia and alcohol in most cases. The former component is present for the halogenide anions to migrate in the chromatographic layer in the form of ammonium salts<sup>1</sup> and the latter one alone or in combination with other solvents forms the solvent system. Out of the alcohols methanol, 1-butanol and 2-propanol are used most frequently. It is obvious that choice of the solvents is affected by tradition, the mixtures common in current chromatographical praxis being chosen.

Our previous comparison<sup>2</sup> of some recommended eluent systems for chromatographical separation of inorganic iodine compounds indicates that different behaviour of various oxidation degree of iodine on a silica gel thin layer depending on composition of the eluent system is affected mainly by the choice of the alcohol for the given system. This factor has not yet been systematically studied, and the present report summarizes our results of investigations of the effect of quality and quantity of alcohol in the eluent system alcohol-ammonia on chromatographic separation of iodide, iodate and periodate.

### EXPERIMENTAL

All the used chemicals and solvents were *p.a.* purity grade, redistilled water was used for preparation of the solutions. Concentrations of the stock solutions were determined by usual analytical procedures. The experiments were carried out with the individual valence forms of radioiodine  $^{131}I$  in trace concentrations. The  $^{131}I^-$  was used in the form of  $K^{131}I$ : we used either directly commercial samples of  $K^{131}I$  (USSR) of specific activity within 260 to 370 MBq . ml<sup>-1</sup> containing, according to the dates of the manufacturer, 97 to 99% KI, about 1% of the formed  $^{131m}Xe$ , <0.01% other radioisotope admixtures, <0.1 mg  $SO_4^{2-}$  . ml<sup>-1</sup>, <0.01 mg Te . ml<sup>-1</sup>,

or we used the same samples with addition of  $\text{Na}_2\text{SO}_3$ , so that all the present higher oxidation states of iodine were reduced to iodide<sup>3</sup>. The  $^{131}\text{IO}_3^-$  was prepared from  $\text{K}^{131}\text{I}$  by oxidation with  $\text{NaClO}$  in acid medium, the  $^{131}\text{IO}_4^-$  was prepared by oxidation of  $\text{K}^{131}\text{I}$  with  $\text{NaClO}$  in alkaline medium<sup>4</sup>. The separation was carried out with the use of commercial TLC plates Silufol R (Kavalier Glass Works, ČSSR) consisting of aluminium support and wide-porous silica gel adsorbent with starch as binder. The plates were not physically or chemically modified before use. Standard conditions were used for development of the chromatograms. Ascending arrangement was used with the slope of the plates  $\alpha = 0.6$  rad. 50 ml eluent mixture was used for each run, two plates 25.150 mm being developed at once. The development was carried out at room temperature immediately after spotting and drying of the radioiodine sample and was stopped when the solvent front was in the distance 100 mm from the start line. The chromatograms were dried in air, detection of the individual compounds was carried out radiometrically.

## RESULTS AND DISCUSSION

Influence of  $\text{C}_1$  to  $\text{C}_5$  monobasic saturated open-chain alcohols (both with straight and branched chain) was studied at constant ammonium ion concentration ( $c_{\text{NH}_4^+}$ ) and constant volume ratio of organic to aqueous phase ( $\varphi = V_o/V_w$ ). The alcohols having more than five carbon atoms ( $n > 5$ ) are not suitable, as they are slightly miscible or immiscible with water.

The  $R_F$  values of  $\text{I}^-$ ,  $\text{IO}_3^-$  and  $\text{IO}_4^-$  are given in Fig. 1 for various  $n$  of the alcohols used in eluent system ( $c_{\text{NH}_4^+} = 0.5\text{M}$ ,  $\varphi = 9$ ). The used alcohol has no influence

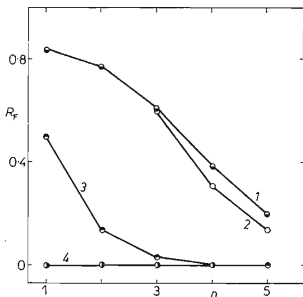


FIG. 1

Effect of Alcohol on  $R_F$  Values ( $n$  number of carbon atoms in the alcohol chain);  $c_{\text{NH}_4^+} = 0.5\text{M}$ ;  $\varphi = 9$

1  $\text{I}^-$ , normal alcohols; 2  $\text{I}^-$ , isoalcohols; 3  $\text{IO}_3^-$ ; 4  $\text{IO}_4^-$ .

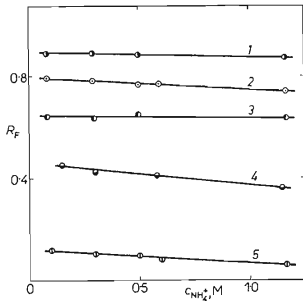


FIG. 2

Relation between  $R_F$  Values and Ammonium Ion Concentration  $c_{\text{NH}_4^+}$  in the System

1  $\text{I}^-$ , ethanol,  $\varphi = 1$ ; 2  $\text{I}^-$ , ethanol,  $\varphi = 9$ ; 3  $\text{IO}_3^-$ , ethanol,  $\varphi = 1$ ; 4  $\text{I}^-$ , 1-butanol,  $\varphi = 9$ ; 5  $\text{IO}_3^-$ , ethanol,  $\varphi = 9$ .

on position of  $\text{IO}_4^-$  spot in the chromatogram which remains at the start line in all the cases. However, the  $n$  values affect markedly the mobilities of  $\text{I}^-$  and  $\text{IO}_3^-$  which both increase with decreasing  $n$ , chain branching of the alcohol being less significant. Iodide migrates faster than iodate, being almost at the solvent front (for low  $n$  values).

The dielectric constants  $\epsilon$  of greater part of the used alcohols are known, the  $\varphi$  value was chosen high enough in the given case, so that it was possible to determine the correlation between  $R_F$  and  $\epsilon$ . This dependence has a course which represents approximately the mirror image of that in Fig. 1. This fact is due to  $\epsilon \sim 1/n$ .

Effect of concentration of the aqueous ammonia solution used for preparation of the alcohol-ammonia eluent mixtures on the  $R_F$  values is given in Fig. 2, where analytical ammonia concentrations ( $c_{\text{NH}_4^+}$ ) in the system are plotted on the  $x$ -axis. The starting concentrations of the aqueous ammonia solutions used were ten times higher than the given  $c_{\text{NH}_4^+}$ , thus the last points at the curves give the values obtained with the concentrated ammonia solutions. Change of the ammonium ion content in the system has an unimportant effect on mobility of the studied anions in the silica gel thin layer, the effect being the lower the less alcohol is present in the eluent system. Regardless of the alcohol used the mobilities of  $\text{I}^-$  and  $\text{IO}_3^-$  slightly decrease with increasing  $c_{\text{NH}_4^+}$ . The dependences in Fig. 2 are important from the practical point of view, especially with respect to instability of aqueous ammonia stock solutions.

Behaviour of  $\text{I}^-$  and  $\text{IO}_3^-$  is strongly affected by change of volume ratio of the organic to aqueous phase of the system, *i.e.* by the change of  $\varphi$ . From Fig. 3 it is obvious that mobility of  $\text{IO}_3^-$  is much more sensitive to the change of  $\varphi$  than mobility of  $\text{I}^-$ . For both  $\text{I}^-$  and  $\text{IO}_3^-$  the  $R_F$  values are decreased with increasing  $\varphi$ . The effect is the more marked the greater is the difference between dielectric constants of water and the alcohol used. Decreasing  $\varphi$ , especially in the range  $0 < \varphi < 1$ , makes the separation of  $\text{I}^-$  and  $\text{IO}_3^-$  worse, which is due to decrease of mobility differences between the two anions with increasing amount of aqueous phase in eluent mixture.

Under the chosen experimental conditions (Fig. 3) the least mobility difference was observed for  $\varphi = 0$ , *i.e.* for elution of the chromatograms with 0.5M aqueous ammonia. The eluent system ammonia-water attracted considerable attention recently: Japanese authors<sup>5,6</sup> found that this system, under certain conditions, can separate well  $\text{I}^-$  and  $\text{IO}_3^-$  in TLC with alumina as adsorbent and plaster (of Paris) as binder. They report a somewhat different way of development: first saturation of alumina with ammonia vapours and then development with pure water, but in the communication<sup>5</sup> the authors state that the same results were obtained with mixtures water- $\text{NH}_4\text{OH}$ . Therefore, we investigated the changes in behaviour of  $\text{I}^-$  and  $\text{IO}_3^-$  in TLC with silica gel adsorbent caused by changes of  $\text{NH}_4^+$  ion concentration. Results of our experiments showed that iodide ions migrate in the silica gel thin

layer in the same way as in alumina TL, *i.e.* almost with the front of the elution solvent. On the contrary, silica gel thin layers exhibited only small differences between mobilities of  $I^-$  and  $IO_3^-$ . The differences in  $R_F$  values of  $I^-$  and  $IO_3^-$  ( $\Delta R_F = R_F^{I^-} - R_F^{IO_3^-}$ ) obtained on development of the chromatograms in ammonia solutions of various concentrations are as it follows:

$NH_4OH, \text{ mol l}^{-1}$	0.5	3	7	12.6
$\Delta R_F$	0.06	0.06	0.08	0.10

The  $R_F$  values of the both anions show a very slight decrease with  $NH_4OH$  content in solution within this very broad concentration range. The greatest  $R_F$  difference was obtained in concentrated ammonia solutions ( $\Delta R_F$  0.1), however, compared with that obtained with alumina layers<sup>5</sup> ( $\Delta R_F$  0.62) it is practically unimportant from the viewpoint of efficient chromatographical separation of iodide and iodate.

An important criterion in the choice of eluents system is also time  $\tau$  of the development of the chromatogram. It was shown that the alcohol used affects not only the behaviour of the studied iodine compounds in thin layer, but also the course of development of the chromatogram. Generally the development time becomes longer with higher alcohols. For development of chromatograms of constant length it is  $\tau = f(n)$ , which is important *e.g.* for the choice of eluent system for chromatographic separation of various forms of iodine from its fission radioisotopes with relatively short half-lives as *e.g.*  $^{132}I$ ,  $^{133}I$ ,  $^{134}I$  and  $^{135}I$ . The shorter is the transformation half-life of the given radioiodine isotope, the faster must the eluent system advance along the chromatographic layer. The highest velocities were found for the eluent mixtures with methanol (Fig. 4, curve 1), and, therefore, the system methanol–ammonia is the most suitable for quick radiochemical separations. According to

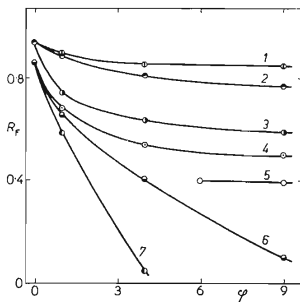


FIG. 3

Dependence of  $R_F$  of Iodide and Iodate on Volume Ratio of Organic to Aqueous Phase ( $\phi$ ) in Eluent System;  $c_{NH_4^+} = 0.5M$   
 1  $I^-$ , methanol; 2  $I^-$ , ethanol; 3  $I^-$ , 1-propanol; 4  $IO_3^-$ , methanol; 5  $I^-$ , 1-butanol; 6  $IO_3^-$ , ethanol; 7  $IO_3^-$ , 1-propanol.

ref.<sup>7</sup> addition of acetic acid to this system increases the  $R_F$  difference between iodide and iodate.

Some results of investigation of kinetics of development of the chromatograms at  $c_{\text{NH}_4^+} = 0.5\text{M}$  and at  $\varphi = 9$  are given in Fig. 4. From the course of the dependences it is obvious that the motion of the development mixtures along the chromatographic layer is not uniform. Rate of the advance of liquid decreases exponentially with increasing distance from the start line, and with our experimental arrangement the measured average velocities in the first centimeter were five times higher than those measured between the 9th and 10th centimeter. Comparison of the development kinetics in various systems made it possible to standardize the time courses of chromatogram development in the individual systems. For certain points at the chromatogram we calculated the degree of reaching of the standard state ( $\eta$ ) as the ratio of the time needed for advance of the solvent front up to the chosen distance  $d$  from the start line to the time of development of the whole 100 mm length of the chromatogram, i.e.  $\eta = t_d/t_{100}$ . The dependence of  $\eta$  on  $d$  (Fig. 4, curve 5) shows that the relative time courses of development do not depend on the choice of alcohol for the eluent system. The given dependence was obtained by plotting the arithmetical means of data of all the studied alcohols; the values in the individual sets fulfill the Grubbs test of extreme deviations, and magnitude of the given points represents the greatest calculated value of the standard deviation, i.e. for  $d = 9$  cm. Identical dependence was obtained from experiments using different slope ( $\alpha = 0.26$  rad) of the plates in chromatographic box. However, course of the dependence is affected (for a given standardized chromatogram length) by the distance of the start line of the substance to be separated from the surface of developing system and (if the distance is constant) by the chosen standardized chromatogram length.

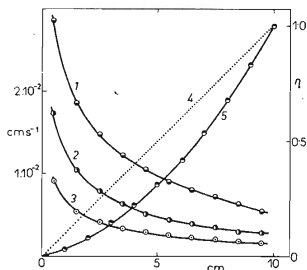


FIG. 4

Dependence of the Solvent Advance Velocity ( $v$ ) on the Distance from Start Line ( $d$ );  $\eta$  the Degree of Reaching of the Standardized State;  $c_{\text{NH}_4^+} = 0.5\text{M}$ ;  $\varphi = 9$

1 The eluent system with methanol; 2 the eluent system with ethanol; 3 the eluent system with pentanol; 4 the theoretical time course of development of the chromatogram for  $v = \text{const.}$ ; 5 the found time course of development for the chromatogram length 100 mm and  $\alpha = 0.6$  rad.

## REFERENCES

1. Achrem A. A., Kuznecova A. I.: *Tonkosloynaya Khromatografia*, p. 155. Izd. Nauka, Moscow 1964.
2. Beneš J., Konůpek M.: *Jad. Energ.* 22, 144 (1976).
3. Beneš J., Konůpek M.: *Jad. Energ.* 22, 251 (1976).
4. Palágyi Š., Zaduban M.: *Radiochem. Radioanal. Lett.* 8, 79 and 89 (1971).
5. Maki Y., Murakami Y.: *Nippon Kagaku Kaishi* 1973, No 1, 85.
6. Maki Y.: *J. Radioanal. Chem.* 27, 33 (1975).
7. Palágyi Š., Zaduban M.: *Chem. Zvesti* 23, 876 (1969).

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