PAPER CHROMATOGRAPHY OF INORGANIC IONS

XVII. THE PAPER CHROMATOGRAPHY OF Pa(V)*

M. LEDERER

Laboratoire Curie, Institut du Radium, Paris (France)

DISCUSSION

In several papers of this series[1] we have been able to show that the data obtained in paper chromatography, apart from their analytical value, may be used to explain the complex chemistry of the elements chromatographed in the same manner as solvent extraction or ion exchange equilibrium results.

The paper chromatography of Pa has so far been mentioned in only two problems, the separation of UX_1 and UZ[2], and the separation of ^{233}Pa from Nb[3]. In both separations solvents containing HF were employed. In this paper we shall discuss the behaviour of Pa in mixtures of acetone–HCl–water.

This study was commenced with the aim of increasing the amount of data on the paper chromatography of tetravalent cations. As only very few solvents had been studied for tetravalent U and no separation noted between U(IV) and Th(IV), we first looked for a solvent that gave a good R_F difference for the mixture U(IV)–Th(IV). Acetone containing 5% water and 5% conc. HCl gave a good separation in these preliminary tests, while other solvents such as acetone–H_2SO_4, butanol–HCl, butanol–HBr (for the last two see[1]), did not yield notable R_F differences.

The solutions of U(IV) in this work were prepared by shaking a solution of uranyl chloride in the required concentration of HCl with a few ml of zinc amalgam in a micro separation funnel and pipetting off an aliquot just before placing it on the paper. Since Pa lies between U and Th in the periodic table, we thought that it might be possible to obtain a reduction (at least partially) of the Pa(V) if it were added to the zinc amalgam reduction with the uranyl chloride; the reduced U(IV) might exert a protective influence on the Pa(IV) during manipulation. Later experiments proved that this was not the case; however, the first chromatograms showed that there was a distinct difference between the movement of ^{233}Pa tracer shaken with U and zinc amalgam and the pure ^{233}Pa tracer.

Oxidation of the U(IV) with dichromate, ferric chloride, and other oxidants, had a profound influence on the movement of the Pa in these solutions, and since
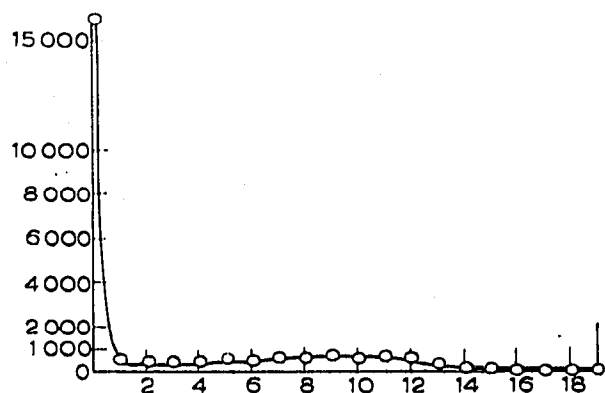
Fig. 1. ^{233}Pa tracer dissolved in 6 N HCl and developed with acetone–HCl–water (90:6:4).
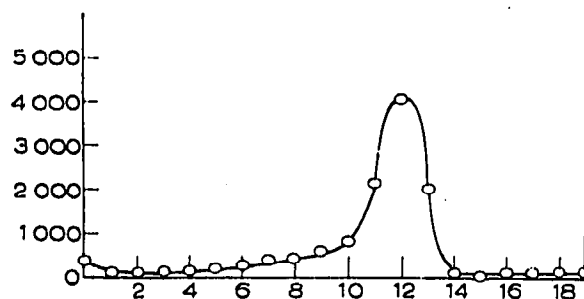

Fig. 2. ^{233}Pa tracer mixed with uranyl chloride in 6 N HCl and shaken with Zn/Hg. Mixture developed with same solvent as in Fig. 1.
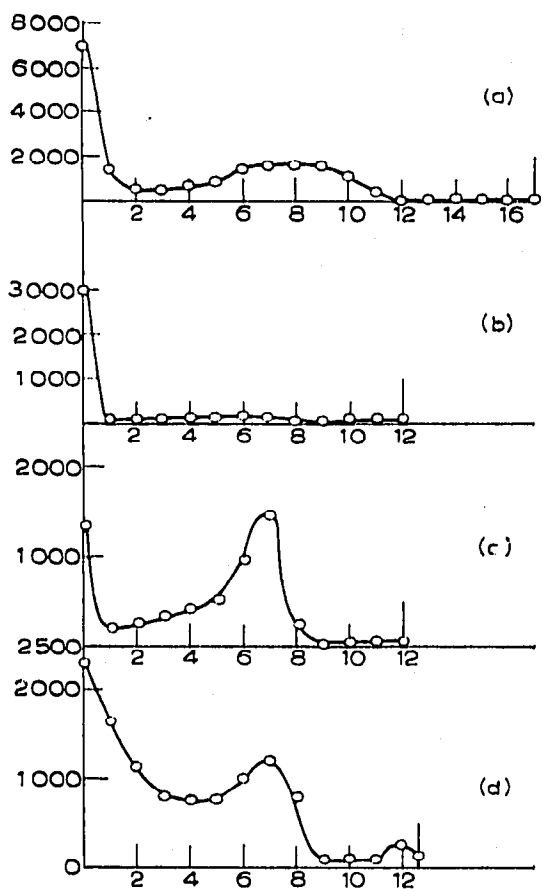

Fig. 3. (a) Solution of Fig. 2, with excess KMnO$_4$ added and developed with same solvent. (b) Solution of Fig. 2, with excess K$_2$Cr$_2$O$_7$ and developed as before. (c) Solution of Fig. 2, with excess FeCl$_3$ and developed as before. (d) Solution of Fig. 2, with excess KClO$_3$ and developed as before.
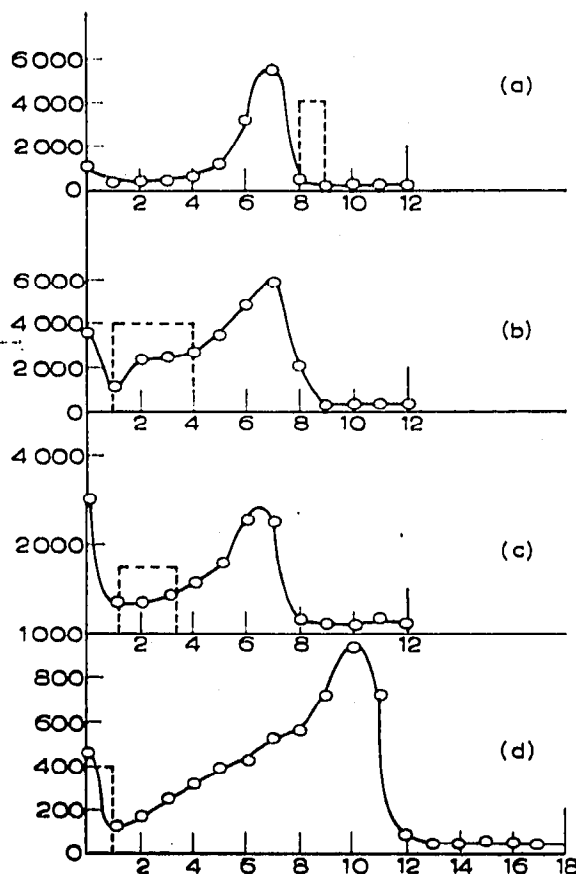

Fig. 4. (a) Solution of ^{233}Pa tracer as used in Fig. 1, mixed with an aerated solution of UCl$_4$ in 6 N HCl and chromatographed with acetone –HCl–water (90:6:4). (b) As in (a), with ZrCl$_4$ solution instead of UCl$_4$ solution. (c) *Idem*, with VCl$_4$ solution instead of UCl$_4$. (d) *Idem*, with ThCl$_4$ solution instead of UCl$_4$.

the position of the Pa was between Th and U(IV), the presence of Pa(IV) was at least considered a possibility. Further experiments showed that simple mixing of U(IV) with the Pa tracer or mixing with other tetravalent ions such as V(IV) or Zr(IV) had the same effect on the behaviour of Pa on the paper. Hence, the effect of mixing with U(IV) solutions or tetravalent ions in general seems to be one of desorption from the paper.

Numerous ions were then examined in mixtures of acetone with increasing concentrations of HCl and corresponding decrease of H_2O concentration. The R_M–pCl relationship is a straight line for all ions tested. While the slope of the line must necessarily be in relation to the number of Cl groups in the metal-chloride complex we have not enough results to identify the species of the complexes formed. However, the graph of R_M plotted against pCl permits the calculation of the optimum separation for a given mixture.

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

The ascending method of development was used throughout this work with large jars covered with watchglasses. Since in mixtures of acetone and HCl the temperature and probably the equilibrium of the atmosphere (which depends on the temperature) change somewhat from day to day, all experiments comparing various concentrations of HCl were performed in series that were started simultaneously.

The solutions that were placed on the paper were prepared by dissolving the chloride of the element (usually 2 g/100 ml) in $6N$ HCl. Spots of about 5 μl were placed on the paper (Whatman No. 1) and developed after standing for a few minutes; this did not allow complete drying of the spots.

I. The behaviour of ^{233}Pa tracer

Fig. 1 shows the activity distribution when a solution of ^{233}Pa tracer in $3N$ HCl is developed with acetone–HCl–water (90:5:5). Of the total of about 20,000 counts/15 sec, about 10% move with the solvent in an ill-defined trail, while 90% remain at the point of application.

Fig. 2 shows an aliquot of the same solution of ^{233}Pa, which was mixed with a solution of uranyl chloride and shaken for a few minutes with Zn/Hg. It is interesting to note that there is still not a symmetrical elution curve but a distinct backward trail to the point of application. When this solution is reoxidised with $KMnO_4$, $K_2Cr_2O_7$, $FeCl_3$, or $KClO_3$, the elution of the Pa tracer again resembles that of the original solution as shown in Fig. 3 (a–d). However reversion of properties seem to be due rather to a strong adsorption as soon as oxidation removes tetravalent ions from the solution than to a reduction to a lower valency of Pa. This could be demonstrated by chromatographing the Pa tracer in mixtures with various tetravalent ions as shown in Fig. 4. Here the U(IV) solution had been well aerated and should have been at a potential well above that necessary for reducing Pa(V). The somewhat lower desorbing ability of Th(IV), Zr(IV) and V(IV) is probably due to the fact that the differences between their R_F values and the R_F value of Pa are greater, and thus

they do not move together with Pa throughout most of the development, as is the case with U(IV).

II. Measurement of R_F values of tetravalent ions with increasing concentration of HCl

The series of solvents studied was acetone containing 10% of aqueous HCl of increasing acidity. Fig. 5 shows the movement of Pa when mixed with U(IV), in solvents ranging from 2.5 N to 12 N HCl. Tables I and II show the R_F values of Pa and numerous other cations.

R_F values were measured with reference to the *water front*. Zr(IV) behaves differently according to its origin. Solutions of $ZrOCl_2$ (pure, Merck) dissolved in cold 6 N HCl gave round spots with a slightly diffused rear edge. Samples of ZrO_2 and $ZrCl_4$ (which were found in our laboratory) when dissolved in HCl either hot or cold yielded usually one spot at the point of origin joined with a spot of the usual R_F value by a more or less pronounced comet. This may offer a method for detection of the formation of colloidal ions in solutions of Zr(IV).

III. Interpretation of results

The formation of a chloride complex of a metal ion

$$M(H_2O)_x^{y+} + xCl^- \rightleftharpoons MCl_x^{(y-x)+} + xH_2O \qquad (1)$$

when reversible will give the mass action equation

$$K = \frac{[MCl_x] \cdot [H_2O]^x}{[M(H_2O)_x] \cdot [Cl^-]^x} \qquad (2)$$

In those cases where the complex is a cation of diminished charge, a neutral substance, or a weak acid (examples of each type are $FeCl^{++}$, $FeCl_3$, and $HFeCl_4$), it may be assumed that the partition coefficient of the complex favours the organic phase, while that of the free ion usually favours the aqueous phase.

Thus the partition coefficient of a metal ion in equilibrium with its chloride complex will in such cases vary directly with the amount of complexation. If we then express eqn. (2) in the form:

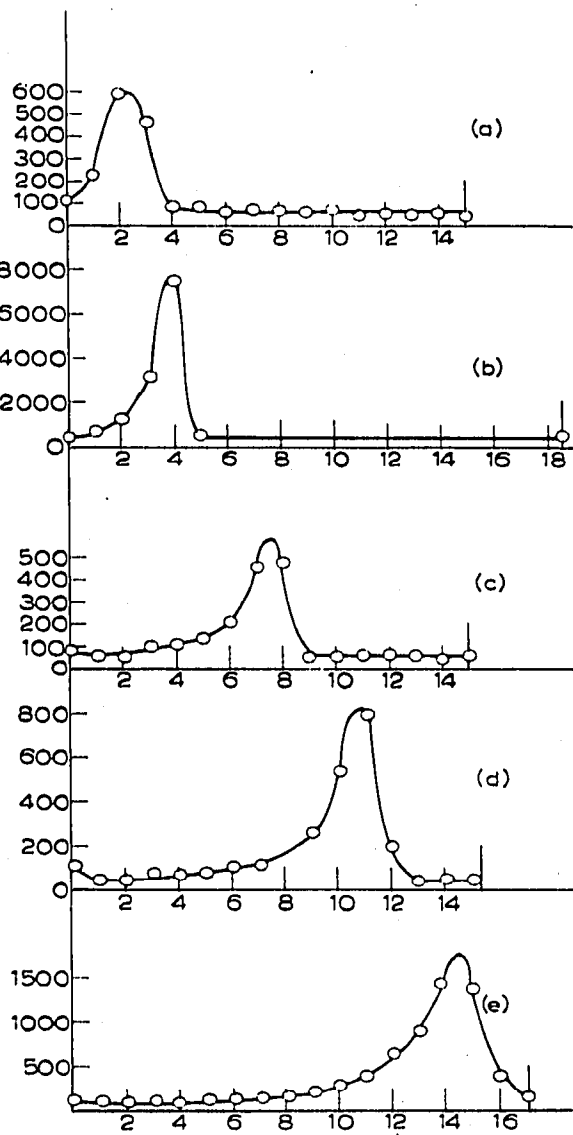$$-pK = \log \left[\frac{MCl_x}{M(H_2O)_x}\right] + x \log [H_2O] + pCl^- \qquad (3)$$

Fig. 5. Mixtures of UCl_4 and ^{233}Pa tracer developed with various mixtures of acetone, HCl and water. The activity curve represents only the ^{233}Pa.

	(a)	(b)	(c)	(d)	(e)
Acetone	90	90	90	90	90
HCl conc.	3.5	5	6	8	10
Water	6.5	5	4	2	—

we see that the log $\left[\dfrac{MCl_x}{M(H_2O)_x}\right]$, which is then the log of the partition coefficient

will vary as the pCl⁻ and the log [H₂O]. In most chromatographic solvents these two variables vary simultaneously and independently: when, for example, butanol is saturated with HCl of various concentrations it will also dissolve more water, as is usually evident from the amounts of the two phases obtained. In the mixtures of acetone–HCl–water examined, the water concentration is varying inversely with the HCl concentration of the solvent; thus the effect of progressive dehydration and complexation proceed to the same extent and we may rewrite eqn. (3).

$$- pK = \log \left[\frac{MCl_x}{M(H_2O)_x}\right] + 2x\,pCl^- \tag{4}$$

Thus, when in eqn. (1) the value for x is constant for a given range of HCl concentration then $\log\left[\dfrac{MCl_x}{M(H_2O)_x}\right]$ will vary directly with pCl. The only measure of the log of the partition coefficient that can be obtained from the R_F value is the R_M value $\left(R_M = \log\left(\dfrac{1}{R_F} - 1\right)\right)$, whcih as we have shown for similar systems varies directly with $\log\left[\dfrac{MCl_x}{M(H_2O)_x}\right]$ (see eqn. (4)).

We may write $\qquad - pK = R_M + 2x\,pCl^- + K \tag{5}$

where K is a constant of the chromatographic system.

When the results of Tables I and II are used to plot R_M against pCl, straight lines are obtained for all cases where the order of accuracy of the R_F measurement is sufficiently high, i.e. except for the very high and very low R_F values. Figs. 6 and 7 show this relationship for the tetravalent and for some other cations. Here we see that Mn⁺⁺, Co⁺⁺, U(IV), Pa(V) and Zr(IV) vary with the same slope, i.e. with the same number for x in eqn. (4) while V(IV) has x one third as great as these other ions. Then there are some ions, such as Ti(IV), Be⁺⁺ and Th(IV), where the

TABLE I

R_F VALUES OF Pa(V) AND TETRAVALENT CATIONS

Solvent			Pa(V)	U(IV)	Th(IV)	Zr(IV)	Ti(IV)	V(IV)
Acetone	HCl	Water						
90	2.5	7.5	0	0.05	0.012			
90	3.5	6.5	0.17	0.23	0.013			
90	5.0	5.0	0.31	0.52	0.018	0.10	0.095	0.165
90	6.0	4.0	0.49	0.58	0.017	0.28	0.11	0.19
90	7.0	3.0				0.43	0.10	0.224
90	8.0	2.0	0.68	0.80	0.028	0.55	0.12	0.27
90	9.0	1.0		0.86		0.61	0.12	0.29
90	10.0	0	0.84	0.98	0.053			

TABLE II
R_F VALUES OF VARIOUS ELEMENTS

Solvent			Ni^{++}	Mn^{++}	Co^{++}	Cu^{++}	Be^{++}	Sr^{++}	Ba^{++}	Al^{+++}	Mo^{VI}	SeO_3^{--}	TeO_3^{--}	UO_2^{++}
cetone	HCl	Water												
90	3	7			0.47	0.89								1.0
90	4	6	0.029	0.33	0.62	0.93	0.27	o	o		WF-LF	LF	WF	1.0
90	5	5								0.019				
90	6	4	0.034	0.52	0.78		0.28	o	o	0.031	WF-FL	LF	WF	
90	7	3				0.97				0.035				1.0
90	8	2	0.02	0.71	0.90	WF	0:26	o	o	0.026	WF-LF	LF	WF	
90	9	1								0.036				
90	10	0	0.02	0.78	0.98	WF	0.21	o	o		WF-LF	LF	WF	

WF   = moves on the water front.
LF   = moves on the liquid front.
WF-LF = moves between water and liquid front.

slope is slightly positive or negative depending on the exact conditions of the development. It appears certain that no change in complexation occurs with these ions.

We believe that this is the first paper chromatographic system in which a correlation between R_F value and the composition of the solvent has been found for inorganic ions. This correlation should yield information as to the formula of the complex. However, there are still too many unknown factors, such as the state of the ion at the beginning of the straight-line relationship, for one to be able to study complexes by chromatographic methods. From equation (5) it also appears possible to obtain a measure of the instability constant of a complex; however, this would only be
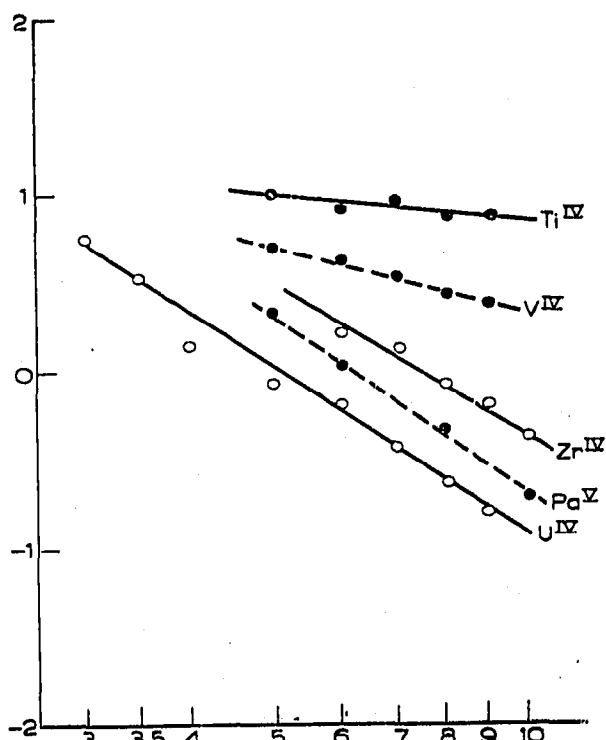

Fig. 6. Graph of R_M values plotted against pCl for Pa(V) and tetravalent cations.
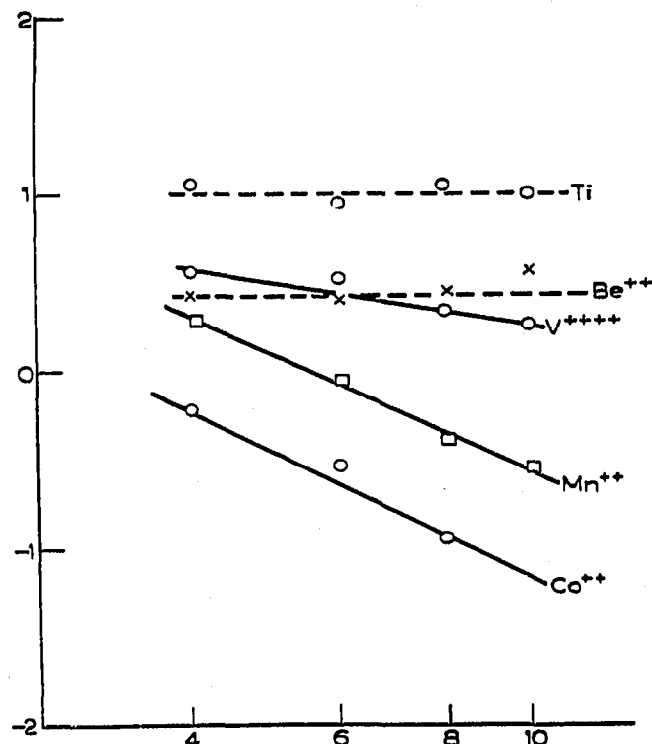

Fig. 7. Graph of R_M values plotted against pCl for several cations.

possible if one could assume that the partition coefficient depends only on complexation and not also on the solubility of the free and the complex ions in the various solvents.

The most important application that we can suggest for this correlation lies in the possibility of calculating in which region we can obtain the best separation of a given mixture.

When two R_M–pCl lines are parallel the best separation may be obtained when both R_M values are nearest to R_M o; when they are divergent the greatest R_M difference yields the greatest R_F difference.

SUMMARY

The paper chromatography of Pa(V) in acetone–HCl–water mixtures has been studied. The movement of Pa(V) as well as of other cations may be expressed by the equation

$$-pK = R_M + 2x\, pCl^- + K$$

providing the ratio acetone to HCl + water is constant (90:10).

REFERENCES

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