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## THIN-LAYER CHROMATOGRAPHY METHOD FOR THE INVESTIGATIONS OF Re(VII), Mo(VI) AND V(V) IONS MIXTURES

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### ABSTRACT

The behaviour of Re(VII), Mo(VI) and V(V) ions was studied chromatographically in aliphatic alcohol-HCl systems on  $Al_2O_3$  as an adsorbent. Changes in the chromatographic process with the changes of the kind and composition of mobile phase were analysed.

It was also attempted to describe theoretically the results of chromatographic separation by using the thermodynamic theory of adsorption from multicomponent solutions.

### INTRODUCTION

The possibility of the use thin-layer chromatography method in analysis of inorganic ion mixtures has been studied in this

paper. Studies were carried out on the behaviour and separation possibilities of rhenium(VII), Molybdenum(VI) and vanadium(V) ions in solvent systems of the type aliphatic alcohol - concentrated HCl by using aluminium oxide as adsorbent.

An attempt was also made at theoretical description of the results of chromatographic separation of the above ion mixtures using the thermodynamic theory of adsorption from multicomponent solutions (2,3).

As shown by the results obtained, thin-layer chromatography method is exceptionally useful in studies of inorganic ion mixtures because of a number of advantages, i.e., simplicity of experiment, a short time of analysis, its low cost and because of possible continuous follow up of chromatographic process. The obtained data are interesting not only from analytical reasons but they may also be the basis in optimization of chromatographic separation conditions both for thin-layer and column chromatography, and they are also helpful in studies on the mechanism of the chromatographic process.

#### METHODS

The experimental data presented in this paper were obtained by thin-layer chromatography method. Aluminium oxide Sklarny Kovalier Votice, Czechoslovakia with layer thickness of 0.5 mm was used as an adsorbent. As mobile phases were used pure aliphatic alcohols: methanol, ethanol, propanol, butanol, iso-butanol, pentanol and iso-pentanol and concentrated HCl, as well as mixtures alcohol - HCl with different volume ratios.

Solutions of Re(VII), Mo(VI) and V(V) ions at concentrations of 1-2 mg l<sup>-1</sup> of each of them were prepared from appropriate crystallized ammonia or sodium salts.

A detailed description of the measurements was given elsewhere (1).

Chromatograms were visualized by spraying the plates initially with 10 % solution of  $\text{SnCl}_2$  in 6 N  $\text{HCl}$  and with 50 %  $\text{NH}_4\text{SCN}$  water solution. This procedure resulted in formation of rhodanate complexes of rhenium, molybdenum and vanadium ions of orange, pink and yellow colours, respectively.

### RESULTS and DISCUSSION

Experimentally obtained  $k_M$  values of the ions studied in all mobile phase systems given above are presented in Tables I - VII.

Theoretical  $k_M$  values of the ions were calculated from the equation based on the thermodynamic theory of adsorption from multicomponent solutions (2,3) :

$$k_{M1,2} = \varphi_1 \Delta k_{M1,2} + (\varphi_1^s - \varphi_1) (\Delta R_{M1,2} + A_2) + R_{M2} \quad (1)$$

where  $k_{M1,2}$ ,  $k_{M1}$  and  $k_{M2}$  are  $k_M$  values of a given ion in mixed mobile phase 1 + 2 and in solvents 1 and 2, respectively;

$\Delta k_{M1,2} = k_{M1} - k_{M2}$  is the difference of  $k_M$  values of the ion in solvents 1 and 2 ;  $\varphi_1$  is a volume fraction of a stronger 1 component of mobile phase ;  $\varphi_1^s - \varphi_1$  is the excess adsorption of component 1 of the mobile phase and can be determined from the equation:

$$\varphi_1^s - \varphi_1 = \frac{\varphi_1(k_1 - 1)(1 - \varphi_1)}{1 + \varphi_1(k_1 - 1)} \quad (2)$$

where  $k_1$  is the adsorption equilibrium constant of component 1 of the mobile phase, and can be assumed that  $-\log k_1 = \Delta R_{M1,2}$  (3) ; the value  $A_2$  represents molecular interactions between chromatographed ions and components of mobile phase.

Table I  
 Theoretical ( $R_M^{\text{th}}$ ) and experimental ( $R_M^{\text{ex}}$ )  $R_M$  values of the ions in methanol - HCl  
 mobile phase system

IONS	$\varphi_1$									
	0.0	0.1	0.25	0.75	0.9	1.0	$R_M^{\text{ex}}$	$R_M^{\text{th}}$	$R_M^{\text{ex}}$	$R_M^{\text{th}}$
Re(VII)	0.45	-0.27	-0.38	-0.95	-1.01	-1.06				
Mo(VI)	1.996	0.00	-0.37	-0.83	-0.95	-1.06				
V(V)	1.996	0.09	-0.41	-1.01	-1.12	-1.28				

Table II  
 theoretical ( $r_M^{th}$ ) and experimental ( $r_M^{ex}$ )  $r_M$  values of the ions in ethanol - HCl  
 mobile phase system

IONS	$\xi$										
	0.0	0.1	0.25	0.5	0.75	0.9	1.0				
	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$
Re(VII)	0.41	-0.27	-0.48	-0.87	-0.68	-1.01	-0.96	-1.01	-1.02	-1.06	
Mo(VI)	1.996	0.75	0.42	-0.21	0.19	-0.66	-0.58	-0.75	-0.80	-0.95	
V(V)	1.996	0.60	0.12	-0.57	-0.27	-0.79	-0.73	-0.91	-0.86	-0.95	

Table III  
 Theoretical ( $R_M^{th}$ ) and experimental ( $R_M^{ex}$ )  $R_M$  values of the ions in propanol - HCl  
 mobile phase system

IONS	$\phi_1$									
	0.0	0.1	0.25	0.75	0.9	1.0	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$
Re (VII)	1.12	-0.04	-0.29	-0.48	-0.47	-0.95	-0.96	-1.06	-1.10	-1.20
Mo (VI)	1.996	0.33	0.11	-0.07	-0.09	-0.75	-0.74	-0.95	-0.93	-1.06
V (V)	1.996	1.996	1.51	1.28	1.17	-0.08	0.22	-0.55	-0.52	-0.55

Table IV  
 Theoretical ( $K_M^{th}$ ) and experimental ( $K_M^{ex}$ )  $K_M$  values of the ions in butanol -HCl  
 mobile phase system

IONS	$\phi$													
	0.0	0.1	0.25	0.5	0.75	0.9	1.0							
	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{ex}$	$K_M^{th}$	$K_M^{th}$	$K_M^{th}$	$K_M^{th}$	$K_M^{ex}$	$K_M^{ex}$
Re(VII)	1.996	0.41	-0.57	-0.58	-0.67	-0.87	-0.82	-0.95	-0.97	-1.06	-1.06	-1.12		
Mo(VI)	1.996	0.67	0.80	-0.14	0.47	-0.51	-0.03	-0.41	-0.54	-0.75	-0.86	-1.06		
V(V)	1.996	0.60	0.64	-0.18	0.36	-0.57	-0.09	-0.48	-0.55	-0.72	-0.82	-1.01		



Table V  
Theoretical ( $R_M^{\text{th}}$ ) and experimental ( $R_M^{\text{ex}}$ )  $k_M$  values of the ions in iso-butanol - HCl  
mobile phase system

IONS	$\psi_1$											
	0.0	0.1	0.25	0.5	0.75	0.9	1.0					
	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{ex}}$	$R_M^{\text{th}}$	$R_M^{\text{th}}$	$R_M^{\text{th}}$		
Re(VII)	1.38	0.16	0.10	-0.27	-0.12	-0.87	-0.46	-0.87	-0.79	-0.87	-0.99	-1.12
Mo(VI)	1.996	0.23	-0.15	-0.18	-0.31	-0.53	-0.56	-0.87	-0.51	-1.01	-0.97	-1.06
V(V)	1.996	0.23	0.14	-0.14	-0.06	-0.37	-0.37	-1.01	-0.69	-1.06	-0.88	-1.01

Table VI  
 Theoretical ( $R_M^{th}$ ) and experimental ( $R_M^{ex}$ )  $R_M$  values of the ions in pentanol - HCl  
 mobile phase system

IONS	$\phi_1$											
	0.0	0.1	0.25	0.5	0.75	0.9	1.0					
	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$		
Re(VII)	1.996	0.45	0.11	-0.12	-0.11	-0.39	-0.45	-0.87	-0.79	-1.01	-0.99	-1.12
Mo(VI)	1.996	0.60	0.30	-0.14	0.07	-0.37	-0.31	-0.79	-0.69	-0.87	-0.91	-1.06
V(V)	1.996	0.50	0.25	-0.16	0.04	-0.45	-0.32	-0.60	-0.66	-1.06	-0.87	-1.01

Table VII  
 Theoretical ( $k_M^{th}$ ) and experimental ( $k_M^{ex}$ )  $k_M$  values of the ions in iso-pentanol - HCl  
 mobile phase system

IONS	$\varphi_1$										
	0.0	0.1	0.25	0.5	0.75	0.9	1.0				
	$R_M^{ex}$	$R_M^{ex}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	$R_M^{ex}$	$R_M^{th}$	
Re (VII)	1.69	0.18	0.14	-0.14	-0.06	-0.41	-0.43	-0.48	-0.75	-0.99	-1.12
Mo (VI)	1.996	0.23	0.19	-0.12	-0.02	-0.33	-0.37	-0.55	-0.87	-0.92	-1.06
V (V)	1.996	0.21	0.21	-0.05	0.00	-0.31	-0.34	-0.41	-0.55	-0.87	-1.01

The theoretically calculated  $R_M$  values of the ions studied for all mobile phases used are summarized in Tables I - VII.

On the basis of these data diagrams of the relationship between  $R_M$  values of the ions studied and mobile phase composition were made (Figs 1-7). In all cases a great agreement between the experimental and theoretical  $R_M$  values of the ions studied was obtained in the whole range of mobile phase composition. Divergences between these values are observed sporadically in the range of low concentration of a more strong component of the mobile phase.

Differences between theoretical and experimental  $R_M$  values can also be found in the case of Mo(VI) and V(V) ions in butanol - HCl system (Fig. 4 B,C). They should be interpreted by changes in the chromatographic process, these phenomena will be analysed later.

Similar relationships between  $R_M$  values and mobile phase compositions are observed for all ions studied (Figs 1-7).

High  $R_M$  values for the ions in pure alcohols result from a strong adsorption of the ions by aluminium oxide. The increase of HCl concentration in mobile phase ( $\varphi_1$  increases) causes a reduced adsorption of the ions by  $Al_2O_3$ , which can be seen from the decrease of their corresponding  $R_M$  values. Particularly distinct changes occur in the range  $\varphi_1 = 0.0 - 0.3$  in which the most significant changes in the composition of the surface layer take place.

Re(VII) ions occur in anion form  $ReO_4^-$ , which is strongly adsorbed by positive  $Al_2O_3$  adsorption centers in pure alcohols, and their corresponding  $R_M$  values are very high (6-8). A decrease in  $R_M$  values of Re(VII) ions is observed along the change in the composition of mobile phase, i.e., with in-

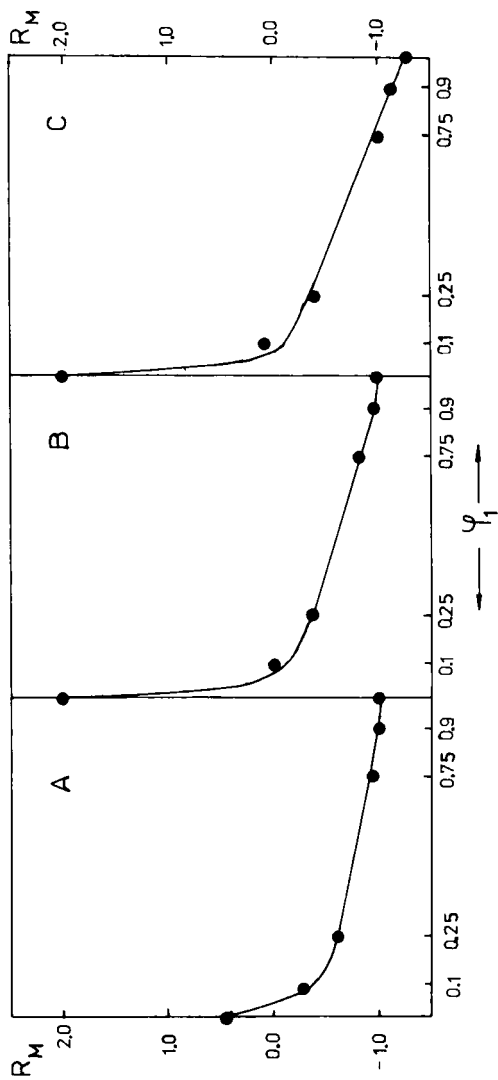


Fig. 1 Dependences between theoretical (lines) and experimental (circles)

$R_M$  values of A - Re(VII) ; B - Pd(VI) ; C - V(V) ions and

methanol - HCl mobile phase composition.

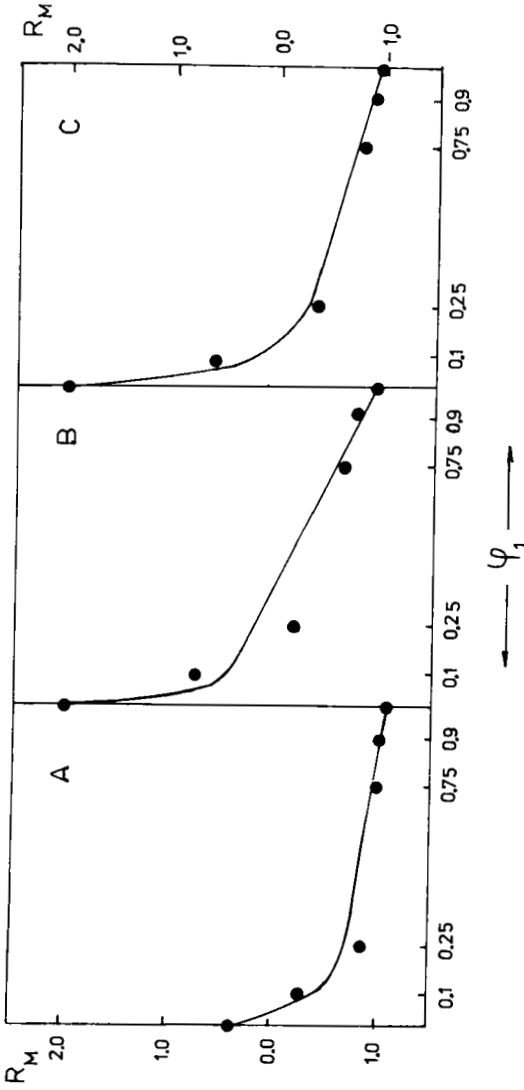


FIG. 5.2 Dependences between theoretical (lines) and experimental (circles)  $R_M$  values of A - Re(VII) ; B - Mo (VI) and C - V(V) ions and ethanol HCl mobile phase composition.

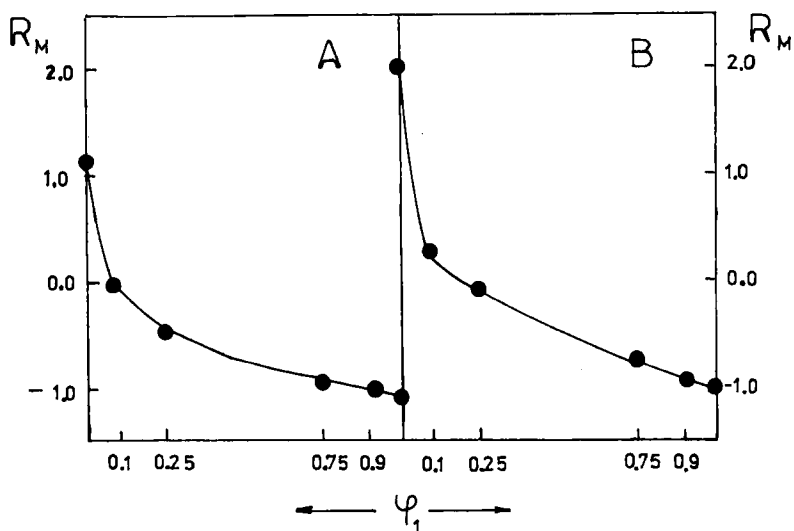


Fig.3 Dependences between theoretical (lines) and experimental (circles)  $R_M$  values of A - Re(VII) ; B - Mo(VI) and propenol - HCl mobile phase composition.

creasing HCl content, Hydrogen ions present in the solution change the solvation step of Re(VII) ions, increasing their adsorption by  $Al_2O_3$  (6,7), and this phenomenon has a decisive effect on the chromatographic process.

At the same time it is very likely that in the chromatographic systems studied,  $ReO_4^{--}$  ions may form complex compounds  $ReO_2Cl_4^{3-}$  (9) which are very weakly adsorbed by  $Al_2O_3$  but are very well dissolved in alcohols. This phenomenon seems to be very probable in the case of using higher alcohols, i.e., pentanol and iso-pentanol (Figs 6,7 A).

In these systems  $R_M$  values of Re(VII) ions change with the change of  $\varphi_1$  in the whole concentration range of mobile phase. For other mobile phases (Figs 1-5 A)  $R_M$  values for Re(VII)

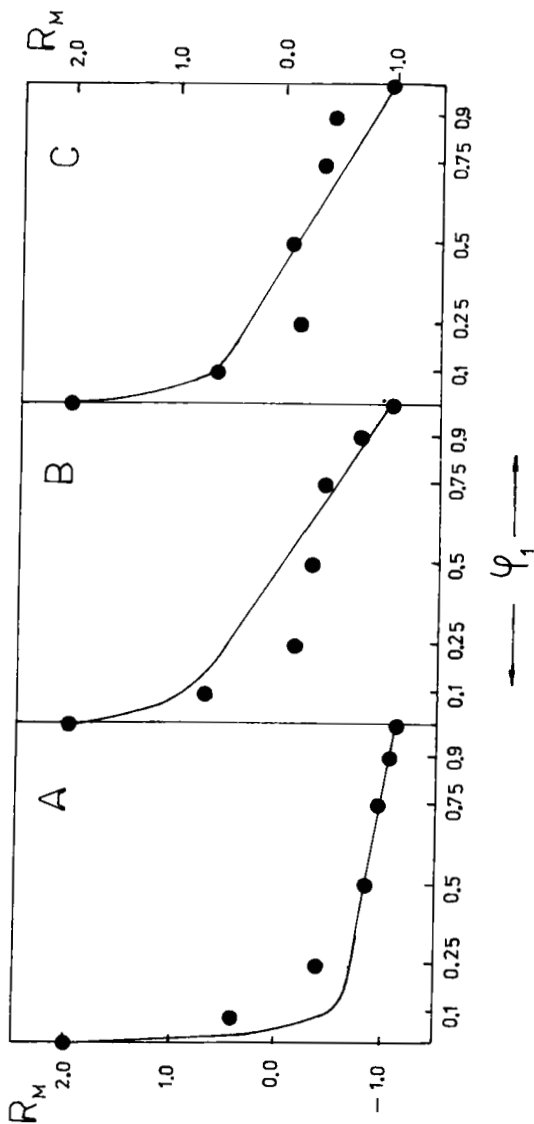


Fig.4 Dependence between theoretical (lines) and experimental (circles)  $R_M$  values of A - Re(VII) ; B - Mo(VI) and C - V(V) ions and but-nel - MCl mobile phase compositor.



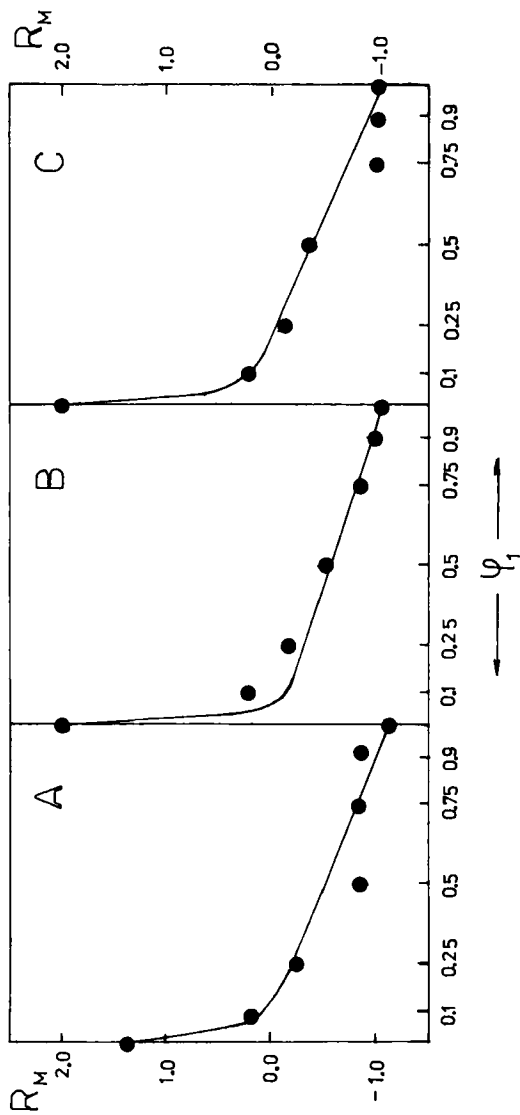


Fig. 5 Dependences between theoretical (lines) and experimental (circles)  $R_M$  values of A - Re(VII); B - Mo(VI) and C - V(IV) ions and iso-butanol - MCl mobile phase composition.

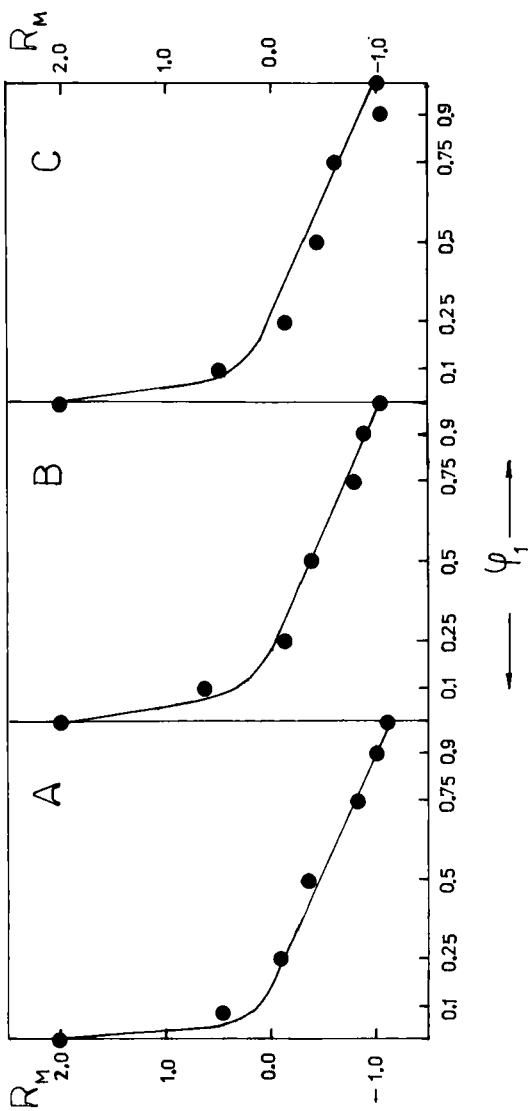


Fig. 6 Dependences between theoretical (lines) and experimental (circles)  $R_M$  values of A - Re(VII); B - Mo(VI) and C - V(V) ions and pentanol - HCl mobile phase composition.

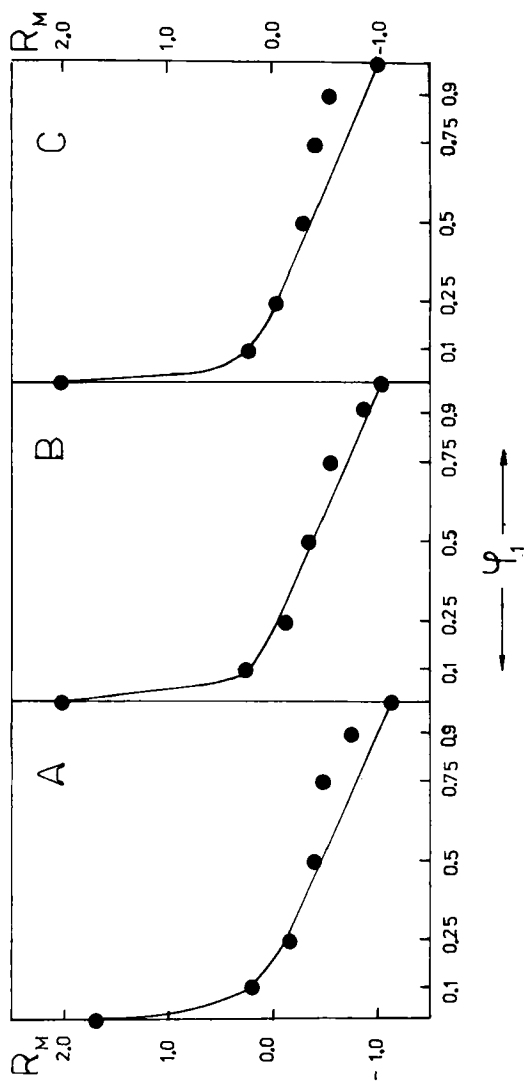


Fig. 7 Dependence between theoretical (lines) and experimental (circles)

$R_M^M$  values of A - Re(VII) ; B - Mo(VI) and C - V(V) ions and iso-pentanol - HCl mobile phase composition.

remain practically constant starting from  $\phi_1 = 0.5$ . However, in the systems pentanol - HCl and iso-pentanol - HCl,  $k_M$  values of the ions change continuously in the whole concentration range of mobile phase.

The chromatographic data of the other ions studied, i.e., Mo(VI) and V(V) suggest that the retention mechanism is the same as in the case of Re(VII) ions.

In studied systems these ions are also anionic form in, i.e. as  $\text{MoO}_4^{2-}$  and  $\text{VO}_3^-$ . Thus in pure alcohols a strong adsorption of these ions is observed on  $\text{Al}_2\text{O}_3$ , which corresponds to high  $k_M$  values (Figs 1-7 B,C). The increase of HCl amount in mobile phase, i.e., the presence of  $\text{H}^+$  ions changes the solvation step of these ions, which is reflected by the decrease of their corresponding  $k_M$  values (10,11).

Furthermore, it seems that in the case of Mo(VI) and V(V) ions a great influence on retention have possible complex formation reactions. From the data presented in the literature (12, 13) it appears that  $\text{MoO}_4^{2-}$  ions may form complex compounds  $\text{MoO}_2\text{Cl}^{2-}$ , which are very well dissolved in alcohols. V(V) ions, however, form  $\text{VO}_2^+$  or  $\text{VO}_3^+$  cations in the given chromatographic systems, which are also weakly adsorbed by aluminium oxide. At the same time these cations form in the presence of  $\text{Cl}^-$  ions oxo-halide  $\text{VOCl}_3$  complexes very well dissolved in alcohols (13).

An analysis of the available data from the literature (10-13) and the retention data obtained in this work accounts for the fact that retention of Mo(VI) and V(V) ions is considerably affected by complex formation which are possible in the given chromatographic systems. This is seen in the constant relationship between  $k_M$  values of these ions and the composition of

mobile phase (Figs 1-7 B,C) . This phenomenon is observed in all mobile phase systems.

Attention should be also drawn to the differences between  $k_M$  values of the ions studied in the systems buthanol - HCl and pentanol - HCl (Figs 4,6) and the corresponding  $k_M$  values of these ions in the systems iso-pentanol - HCl and iso-butanol - HCl in the range of low  $\varphi_1$  values. Smaller  $k_M$  values in the systems with isoalcohols (Figs 5,7) should be interpreted by steric reasons. Alcohols with a branching structure of the carbon chain make adsorption of Re(VII) , Mo(VI) and V(V) ions more difficult than alcohols with a linear structure.

Summing up the results of the studies carried out, it can be concluded that the method of thin-layer chromatography used for analysis of inorganic ions presents a number of interesting data concerning the possibility of separation and optimization of separation conditions of these ions mixtures. It has been also found that the thermodynamic theory of adsorption from multicomponent solutions makes it possible to foresee satisfactory the results of chromatographic separation of mixtures of inorganic ions. which might considerably simplify the selection of optimal conditions of ions separation by thin-layer chromatography. Moreover, it has been found that the retention data may be the starting point in studies on the mechanism of chromatographic process.

The results presented above suggest that in the case of inorganic ions in systems of the type aliphatic alcohol - HCl on  $Al_2O_3$  as an adsorbent this process is considerably affected by complex formation.

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