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A thermochemical study of complex formation in chelating ion-exchange resins

S.V. Kertman *, G.M. Kertman, Yu.A. Leykin

Department of Chemistry, Tyumen State University, Semakov str. 10, 625003 Tyumen, Russian Federation

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Abstract

The process of sorption of transition metal ions from nitrate solutions onto chelating ion-exchange resins containing amino, phosphonic and aminophosphonic acid groups has been studied with the help of a Calvet microcalorimeter. Direct calorimetric measurements were performed at different degrees of exchange and the enthalpy variations for the system were obtained. In this work it is shown what the Irving–Williams rule holds for amino groups containing AS resin. In the case of phosphonic acid groups containing KRF resin, the ΔH of sorption of the transition metal ions depends on the Cartledge ionic potential.

Keywords: Chelation; Ion-exchange resin; Microcalorimetry; Transition metal ion

1. Introduction

Now that chelating ion-exchange resins are being widely used, a physicochemical study of the sorption processes accompanying complex formation is a matter of topical interest. The microcalorimetric method makes it possible to probe the heterogenic sorption process as it occurs, separating this method from spectral ones, for instance, which only permit the study of metal ion and ligand resin group complexes after the sorption process is over and the resin has separated from the

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* Corresponding author.

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Table 1
Resins studied

Resin	Functional group
AS	$-NH_2$
KRF	$-PO_3H_2$
ADF	$-NH-CH_2-PO_3H_2$
ES-467	$-CH_2-NH-CH_2-PO_3H_2$

equilibrium solution. As is already known, the structural changes in ion-exchange resins may continue for up to a few weeks [1].

The present study is a continuation of our previous work on the microcalorimetry of the sorption process onto complex-forming resins [2] and the spectral study of the resin ES-467 [3].

2. Experimental

The resins used were synthesized from the copolymers styrene and divinylbenzine. The functional resin groups are given in Table 1.

The transition metal ions were sorbed from nitrate solutions, because the nitrate ion only slightly affects the sorption enthalpy [4,5]. The sorption enthalpy was measured using a Calvet differentiating microcalorimeter.

A previously moistened resin sample of 0.2 g was placed in the microcalorimeter and, after thermostatting, was brought into contact with a thermostatted solution of transition metal nitrate by stirring the nucleus of the calorimeter. Special cells were used for calibration of the system, which was based on the Joule effect and on the enthalpy of KCl at 298 K up to a concentration of 0.278 mol in 1000 g of H_2O. The value of ΔH was 17 567 $\pm$ 36 J mol^{-1}, which agrees well with the values in Ref. [6]. The initial and equilibrium concentrations of transition metal ions were determined using an AAS-1 atomic absorption spectrometer. The load $\bar{X} = 1$ corresponds to the resin having a maximum sorption capacity in 0.1 M metal nitrate solution.

3. Results and discussion

3.1. Sorption on polyaminostyrene

The sorption of transition metal ions in resins of type AS only occurs via the formation of a coordination bond. The transition metal coordination number is six, but the resin AS amino groups occupy a smaller number of vacant coordinating sites of the central atom. As a result, mixed aquacomplexes are formed. The

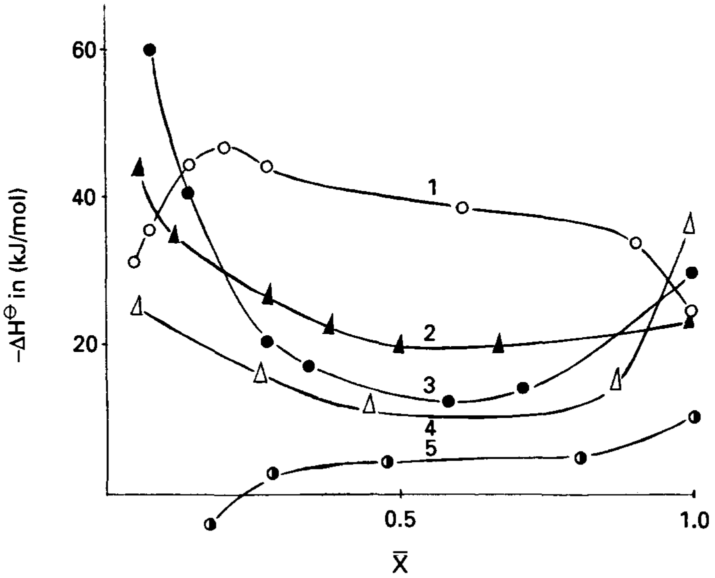


Fig. 1. $\Delta H^{\ominus}$ of partial exchange of metal ions in AS resin: (1) Cu^{2+}; (2) Ni^{2+}; (3) Co^{2+}; (4) Zn^{2+}; (5) Mn^{2+}.

Table 2
ΔH of the transition metal ions and ethylene diamine [10], and AS resin complex formation

Metal ion	ΔH in kJ mol^{-1}	
	Ethylene diamine	AS resin
Mn^{2+}	11.7	3
Co^{2+}	28.9	10
Ni^{2+}	37.2	20
Cu^{2+}	54.5	40
Zn^{2+}	27.8	10

coordination number of the metal ions is most closely approached at low resin loads, causing a sharp rise in sorption enthalpy as $\bar{X} \rightarrow 0$ (Fig. 1). As a result of the difference between the amino group number in the metal coordinating sphere and the transition metal coordination number, a considerable difference in the ΔH value is observed when the number of transition metal ions in the resin AS increases. A certain exothermic increase in the sorption process at large resin loads might be due to ion-pair formation [7], e.g.

$$Co^{2+} + NO_3^- \rightleftharpoons (CoNO_3)^+ \qquad \Delta H = -4.86 \text{ kJ mol}^{-1}$$

An unusual dependence of sorption enthalpy on resin load was observed on studying Cu^{2+} sorption on the resin AS. Usually, the energy discharge is largest at low resin loads, since the concentration of transition metal ions in the ion exchanger is low. In the case of copper ion sorption on aminopolysterene, a decrease in energy discharge as $\bar{X} \to 0$ has been reported. A decrease in energy discharge with increasing number of coordinating bonds between copper ions and amino groups has been reported in the measurement of the enthalpies of copper ion and polyamine complex formation [8,9]. The thermokinetic curve shows an endo effect at the start of copper ion sorption on the AS resin. This may be explained by a large energy expenditure on dehydration of the aquacopper complex, $\Delta H = 19.23$ kJ mol^{-1} [6], or by a large deformation in the AS resin polysterene chains on forming stable copper ions and amino group complexes, which also leads to considerable energy expenditure [8].

The Irwing–Williams rule reflects the changes in the stability constants and in the enthalpies of transition metal complex formation, which follow the trend [10] $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.

Table 2 shows the ΔH values characterizing the equilibrium, as reported in the literature:

$$[Me(H_2O)_6]^{2+} + en \rightleftharpoons [Me(en)(H_2O)_4]^{2+} + 2H_2O$$

$$(en = NH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2)$$

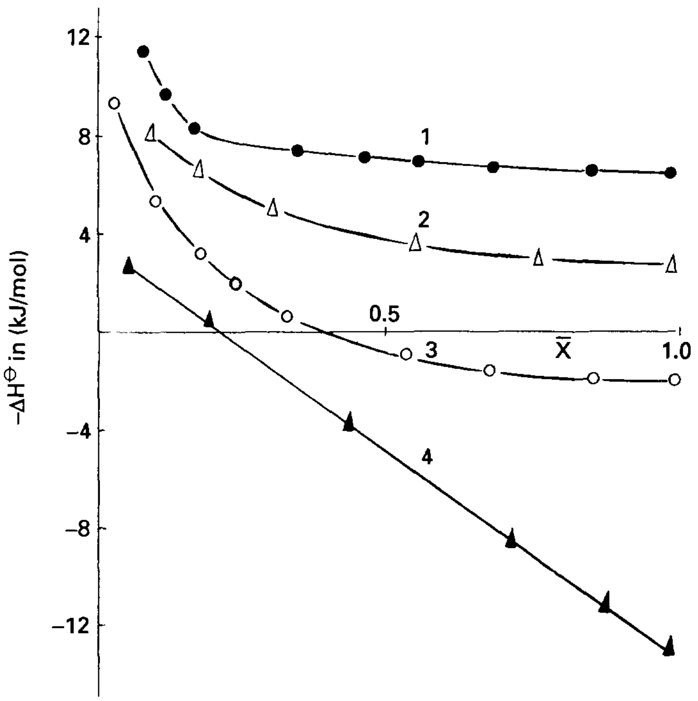


Fig. 2. $\Delta H^{\ominus}$ of partial exchange of metal ions in KRF resin: (1) Co^{2+}; (2) Ni^{2+}; (3) Cu^{2+}; (4) Zn^{2+}.

Table 3
Thermodynamic properties of ions [9]

Ion	Thermodynamic radius in nm	ΔH of hydratation in kJ mol^{-1}
$[CO(H_2O)_6]^{2+}$	0.234	2886.3
$[Ni(H_2O)_6]^{2+}$	0.229	2961.9
$[Cu(H_2O)_6]^{2+}$	0.235	2972.8
$[Zn(H_2O)_6]^{2+}$	0.235	2919.7

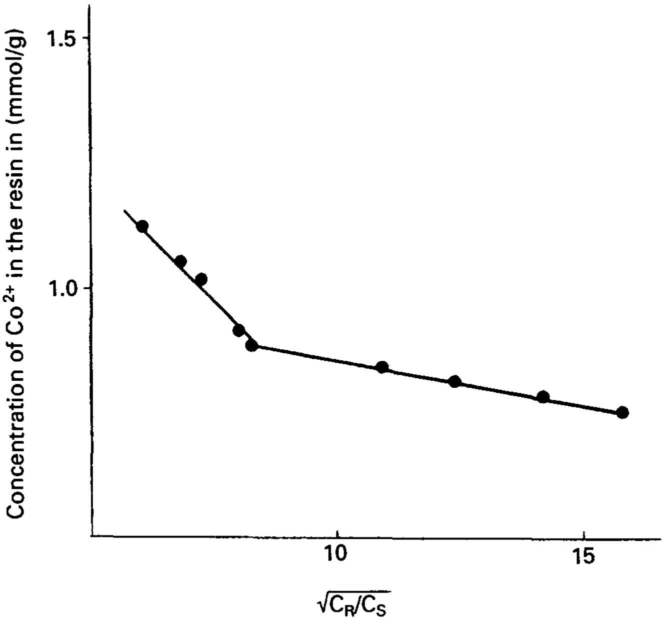


Fig. 3. Sorption isotherms of ion-exchange cobalt ions in KRF resin.

at 25°C for ΔH values of metal ion sorption on the AS resin at intermediate loads. It is obvious from Table 2 and Fig. 1 that the Irwing–Williams rule holds for three-dimensional polyligands, of which the resin AS is one.

3.2. Sorption on phosphonic acid ion-exchange resin

Phosphonic acid ion-exchange resins are moderately acidic and contain active centres of two kinds: phosphonic oxygen and hydroxyl acid groups. The sorption of transition metal ions can proceed via their coordination interaction with the former, and through their ionic interaction with the latter.

When analyzing ion-exchange equilibria it is necessary to take into account not only the nature of the resin and the exchanged cation, but also the nature of the anions. Transition metal ions and anions can form complexes and ionic pairs [1,6,10,11]. The anionic properties affect the condition of transition metal ions in the solution which, in turn, contributes to the sorption energy effect. To eliminate the influence of anions, nitrate solutions were used.

Fig. 2 presents the dependences of the sorption enthalpies of the ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} on the number of the ions sorbed on the cation exchanger KRF. As is obvious from this Figure, the most energy-profitable sorption on the cationic exchanger KRF-5p is by cobalt ions. In the case of nickel ion sorptions, in comparison, an enthalpy sorption alone is observed, whereas in the case of copper ion sorption and zinc ion sorption a change in the values of the energy effect is observed, due to increased metal loading. At small $\bar{X}$, an energy release alone is registered throughout the process, whereas at large $\bar{X}$ a more prolonged energy sorption is observed after short energy release. The energy release at the start of sorption is explained by the primary coordinating interaction between the copper and zinc ions through the fixed cationic exchanger groups. The heat of sorption is not affected so much by the energy expended in deforming the three-dimensional matrix of the resins, or by hydration effects. The thermochemical radius of the hydrated ions and the hydration enthalpies are close, owing to decreasing coordinating interactions.

A considerable change in the metal ion sorption enthalpy, depending on the ion-exchanger load, at small values of $\bar{X}$ is caused by interaction between the sorbed metal ions and the two functional groups of the ion-exchanger.

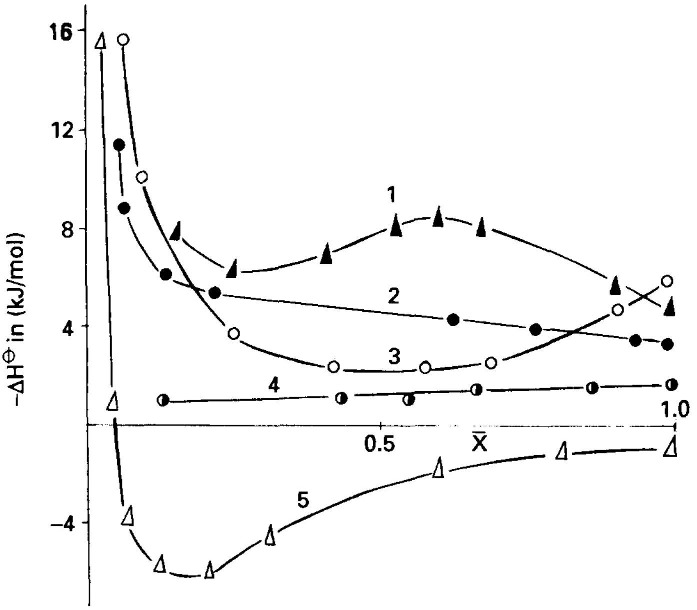


Fig. 4. ΔH^{Φ} of partial exchange of metal ions in ADF resin: (1) Ni^{2+}; (2) Co^{2+}; (3) Cu^{2+}; (4) Mn^{2+}; (5) Zn^{2+}.

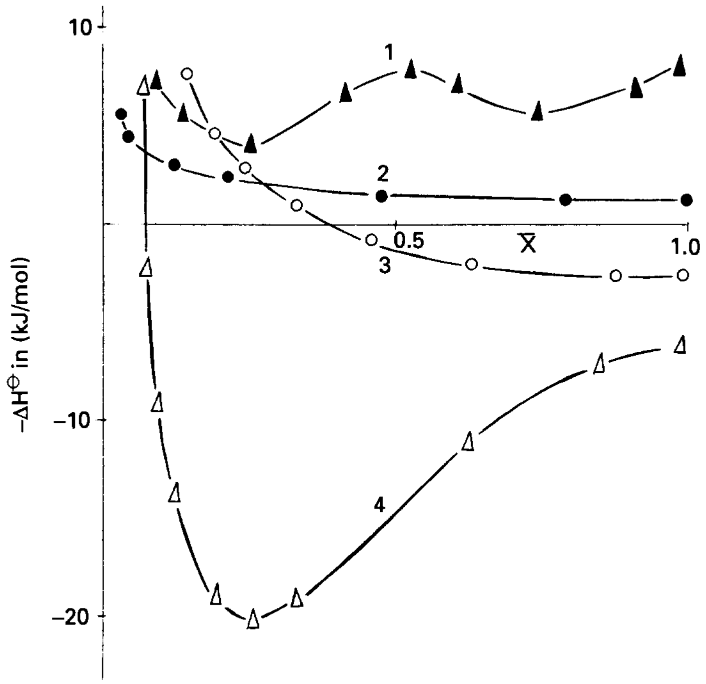
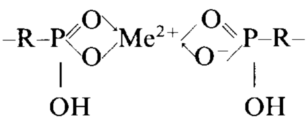
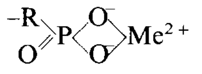


Fig. 5. $\Delta H^{\ominus}$ of partial exchange of metal ions in ES-467 resin: (1) Ni^{2+}; (2) Co^{2+}; (3) Cu^{2+}; (4) Zn^{2+}.

A comparison of sorption isotherms in the coordinates $C_R = f(C_R/C_S)$ (Fig. 3), where C_R = concentration of metal ions in the ion-exchange resin (mmol g^{-1}) and C_S = concentration of metal ions in the solution (mmol ml^{-1}), with $\Delta H = f(\bar{X})$ shows that these dependences have concurring points of inflexion. The presence of an inflexion point suggests a change in the sorption mechanism [12]. At low resin loads, the sorbed ions probably interact with two fixed groups



At high loads, resins can only undergo ionic interaction with one group. Coordination with neighbouring groups, however, cannot be excluded

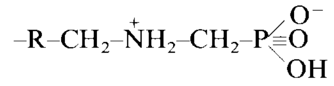


3.3. Sorption on aminophosphonic resins

The polyampholytes ES-467 and ADF belong to the class of aminophosphonic resins. The difference between the two lies in the presence, in the resin ES-467, of a methylene group between the styrenedivinylbenzine matrix and the functional group. These resins can bind metal ions via oxygen atoms from the phosphonic group, and via a nitrogen atom from a secondary amino group [12–14].

The complex stability and change in the sorption enthalpy, on the one hand, follows the Irving–Williams trend [10] $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. On the other hand, with the Cartledge ionic potential [15] increasing in this order, the extent of ionic interaction between the metal ions and ligand groups is expected to increase. This is obvious from Figs. 4 and 5. Within a wide range of loads the enthalpy of sorption increases in the order Mn^{2+}, Co^{2+}, Ni^{2+}, which is in agreement with the Irving–Williams order. Thus the sorption enthalpy of the ions Mn^{2+} and Co^{2-} within a wide range of $\bar{X}$ remains constant. It is only for sorption of Ni^{2+} ions by polyampholites that the maxima are difficult to explain. The copper ion Cartledge ionic potential growth results in (for a wide range of $\bar{X}$) the ΔH of the sorption process being smaller than the ΔH values for Ni^{2+} and Co^{2+} ion sorption. In the case of the chelating ion-exchange resin ES-467 the sorption is endothermic, but this has most influence on Zn^{2-} ion sorption. Aside from the increase in the extent of ionic interaction of the Zn^{2-} ions and the phosphonic polyampholite groups, a decrease in zinc–amino complex formation is in agreement with this. As a result, on sorption of zinc ions, the process is endothermic, and an energy release only takes place at low loads. A decrease in exothermicity, with an increase in copper content in polyampholite, proceeds as the coordination bond number decreases. An increase in the ΔH value at $\bar{X} > 0.5$ for sorption on ADF should be attributed to the effects of copper ions in the solution. With the copper ions diffusing into the ion-exchanger and coordinating with functional groups, the energy required for dehydration decreases, and the total energy of the ion-exchange process increases.

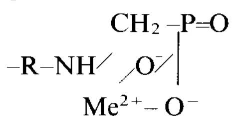
Sorption on ADF of all the transition metal ions studied is energy profitable. This is explained by the fact that in the polyampholyte ES-467, a methylene group is present between the aromatic ring and nitrogen atom. The electron density of the nitrogen atom increases, which enhances its protonation and favours zwitterion structure formation at pH 6 [3]



$-R-CH_2-\overset{+}{N}H_2-CH_2-P(O^-)(=O)(OH)$

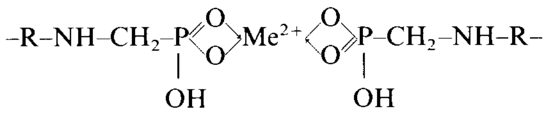
There are fewer coordination active amino groups in the ion-exchanger ES-467 than there are in the ion-exchanger ADF.

At low loads, the ampholite functional groups may act as tridentante ligands, and the complex structure due to sorption could be



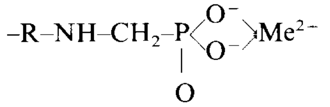
$-R-NH(CH_2-P{=}O)(O)\cdots Me^{2+}-O^-$ (I)

Complexes without amino groups may also be found



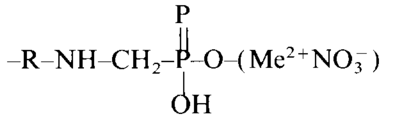
(II)

At large loads, ionic bonding would result in



(III)

In the case of saturated metal nitrate solutions, sorption of ionic pairs can occur



$$-R-NH-CH_2-\underset{OH}{\overset{P}{\overset{\|}{P}}}-O-(Me^{2+}NO_3^-)$$

(IV)

The data obtained agree well with the spectral study of the ion-exchanger ES-467 carried out previously [3].

As stated above, the most energy profitable sorption is that which occurs at the coordinating interaction (I and II). Complexes I and II are formed not only at low ion-exchanger loads, but also at the start of sorption from saturated solutions.

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