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Heats of the immersion of Co^{2+} and Cu^{2+} contained chelating ion-exchange resins

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Abstract

The heats of the immersion of amino, phosphonic and amino phosphonic ion-exchange resins containing different amounts of cobalt or copper ions have been determined with the help of a Calvet microcalorimeter. The adsorption of the water vapour on phosphonic ion-exchange resin in different ionic forms (H^+, Co^{2+}, Cu^{2+}) was studied and enthalpy of the immersion of dry and partially hydrated resins was measured by microcalorimetrical method. The formation of different structures during the water interaction with resin is reflected on the dependence: hydration energy – metal content. The correlation of the ΔH of the immersion and ΔH of the metal ion sorption with the catalytical activity of sorbed complexes of these resins has been shown.

Keywords: Heat of immersion; Ion-exchange resin; Microcalorimetry

1. Introduction

Chelating ion-exchange resins are used as selective sorbents of transition metal ions [1,2] and the immobilized metal ion resins are used as the heterogeneous catalysts [3,4] and as immobilized metal affinity chromatography (IMAC) adsorbents [5,6]. Sorption of the transition metal ions on the chelating ion-exchange resins occurs by the formation of coordination bonds between the sorbed metal ion and ligand groups of the resins. Ion-exchange resins containing two kinds of sorbed ions are considered to be three-component systems in which water is the third component [7]. The interaction of the resin with water is therefore of both practical and theoretical interest.

The enthalpy of sorption of cobalt and copper ions from nitrate solutions on to some chelating ion-exchange resins has been studied earlier [8–10]. However, any ion exchange process is always accompanied by the solvent transfer, water transfer in particular. In the present work the heats of the immersion of amino, phosphonic and amino phosphonic ion-exchange resins containing different amounts of cobalt or copper ions have been determined with the help of a Calvet microcalorimeter. Correlation of the observed data with the catalytical activity of sorbed complexes of these resins has been shown.

2. Experimental

The resins used were based on copolymers of styrene and divinylbenzene. The functional resin

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Table 1
Resins studied

Resin	Functional group
AS	$-NH_2$
KRF	$-PO_3H_2$
ADF	$-NH-CH_2-PO_3H_2;-PO_3H_2$
AMF	$-NH-CH_2-PO_3H_2$

groups are given in Table 1. Cobalt and copper ions were sorbed from nitrate solutions. The initial and equilibrium concentrations of transition metal ions were determined using an AAS-1 atomic absorption spectrometer.

The water-sorption equilibrium of the resins was studied by the isopiestic technique. Resin samples were first dried in a vacuum oven at 100°C for 10 h then transferred to small flat dishes and stored in the vapour atmosphere of desiccators containing various saturated salt solutions which gave different water activities ($a_w = P/P_0$) at 25°C. After 2 months of equilibration the water content of the resins was determined by drying for 10 h at 100°C in a vacuum drying pistol containing phosphorus pentoxide as desiccant.

Dry resins for the calorimetric measurements were handled in a special dry-box filled with nitrogen that had been dried over phosphorus pentoxide.

The sorption enthalpy and enthalpy of the immersion of dry and partially hydrated resins were measured with a differential microcalorimeter of the Calvet type. For sorption measurements a previously moistened 0.2 g resin sample 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. For immersion processes the reaction vessel of the calorimeter was filled with 50 ml of distilled water and the dry or partially hydrated resin sample of 0.1 g was weighed in outgassed thin glass ampoules.

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 17567 ± 36 J/mol, which agrees well with values in Ref. [11]. The load $\bar{X} = 1$ corresponds to the resin with a maximum sorption capacity at 0.1 M nitrate metal solution.

3. Results and discussion

The water vapour sorption isotherms for the resin KRF-5p containing phosphonic acid groups are shown in Fig. 1. It can be seen that at metal forms of the ion-exchange resin the amount of sorbed water is larger than that at the H^+-form. This indicates that the amount of water sorbed by the ion-exchange resin is mainly determined by the following factors: hydration capacity of the counter-ion and the functional group and the resistance of the ion-exchange resin matrix to swelling. The latter limiting of the amount of free water can be neglected as one and the same ion-exchanger is studied in various ion forms. The first factor is practically independent of the crosslinked ion-exchange resin and is determined by the counter ions and functional groups' capacities to hydration. This factor defines the amount of bound water and the change of the thermodynamic functions at sorption [7]. Thus, metal forms of the KRF-5p ion-exchange resin contain the experimental data.

Fig. 2 shows how the immersion energy varies with the initial water content of the ion-exchange resin. The largest differences of energy between the various forms of the ion-exchange resins are observed at small initial amounts of water. If the KRF-5p ion-exchange resin contains more than 2 mmol/g of water, the distinction of immersion energy for all the three forms of the ion-exchange resin is practically not marked. It is probable, that the formation of the water monolayer is completed and only 'free' water is sorbed; the sorption energy of such water is small and the nature of the counter ion no longer affects the immersion energy. The dependence of the resin hydration energy value on the former containing water has a bend, which is conditioned by two stages of the hydration process. The first stage is the 'tied,' water sorption and the second is the 'free' water sorption. Every stage is characterized by its own heat effect. The equation showing the heat effect dependence on the former water content in the resin has been obtained. It enables us to definite the 'tied' water amount. For example, in the phosphonic cationite KRF there is one water molecule for two phosphonic acid groups, it is bound with greater energy than the heat motion energy. The energy spent for stretching the polymer matrix of the ion-exchange resin KRF-5p in H^+-form at its swelling in water exceeds the hydration energy.

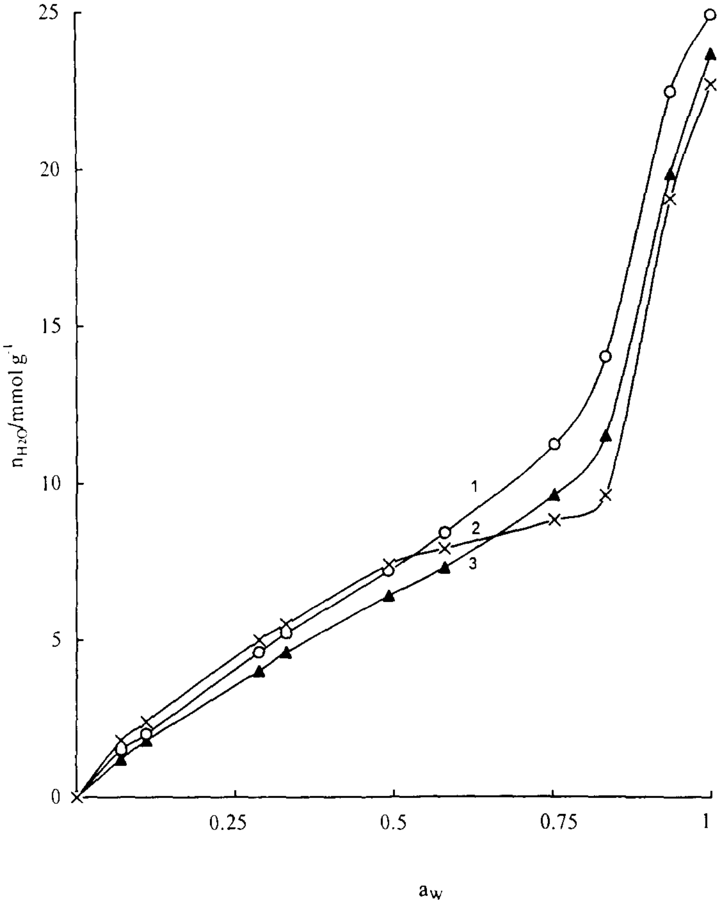


Fig. 1. Water sorption isotherms of (1) Co^{2+}; (2) Cu^{2+} and (3) H^+ forms of KRF resins.

Therefore, the immersion energy of water saturated ion-exchange resin in H^+-form at $a_w = P/P_0 \rightarrow 1$ is positive.

The reaction of hydration, the energy effect of which is measured calorimetrically, can be illustrated by the equation:

$$R - Me^{2+} + (n + m)H_2O \rightleftarrows R{-}Me^{2+}(n + m)H_2O;\ \Delta H_1$$

when a perfectly dry ion-exchange resin is measured and with the equation:

$$R - Me^{2+}mH_2O + nH_2O \rightleftarrows R{-}Me^{2+}(n + m)H_2O;\ \Delta H_2$$

for a partially hydrated ion-exchange resin. Using these energies measured by the immersion technique the enthalpy change for the ion-exchange resin hydration from perfectly dry state to a given humidity can be obtained by the application of Hess' law [12]:

$$R - Me^{2+} + mH_2O = R \rightleftarrows Me^{2+}mH_2O;\ \Delta H_3$$

$$\Delta H_3 = \Delta H_1 - \Delta H_2.$$

Calculated values of ΔH_3, the enthalpy of partial hydration, are shown in Fig. 3.

Fig. 4(a) shows how the heat of immersion of the ion-exchange resin KRF-5p varies with the content of Co^{2+} or Cu^{2+} ions. The immersion energy increases linearly over a wide range of loading of the resin phase by metal ions.

The expression:

$$\Delta Hhydr. = n\Delta H^{RH} + (1 - n)\Delta H^{RMe}$$

is valid for these portions of the curve, i.e. additivity of

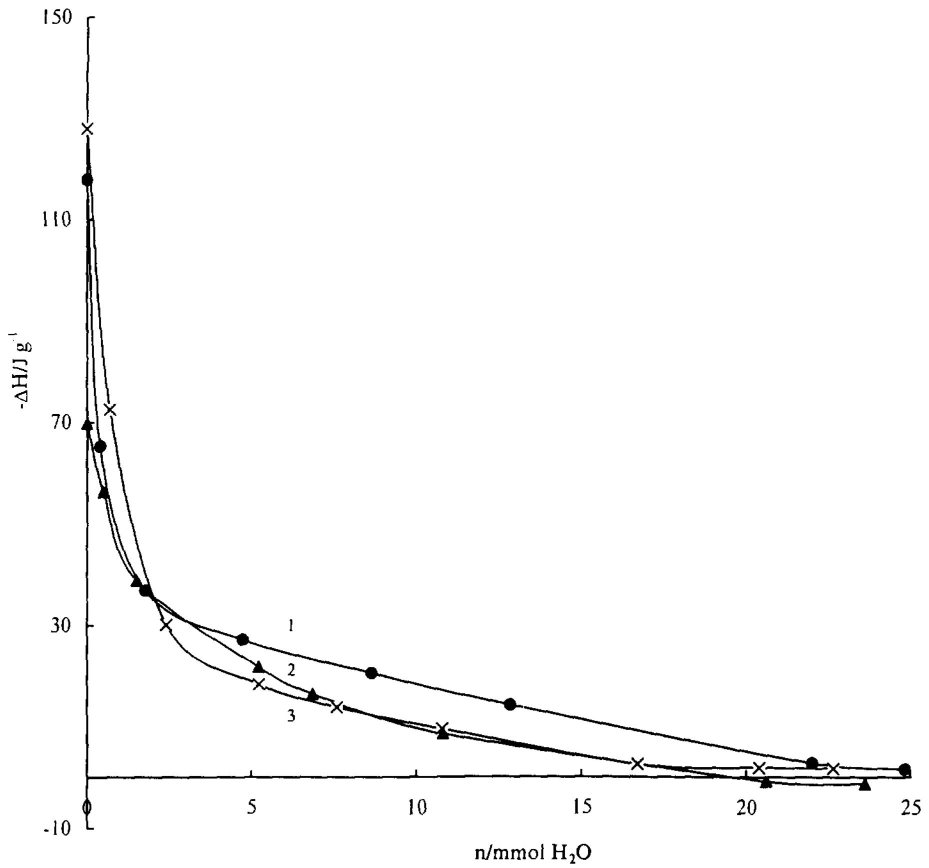
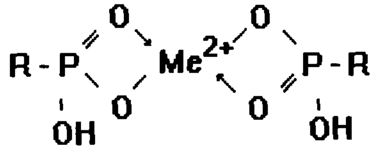
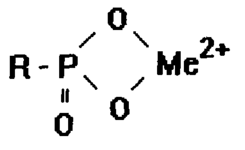
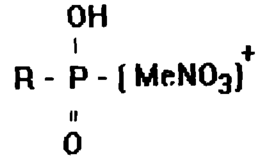


Fig. 2. Heats of immersion of partially hydrated (1) Co^{2+}; (2) H^+ and (3) Cu^{2+} forms of KRF resins.

the immersion energies of H^+ and metal forms of the ion-exchange resin is observed. Deviations from linearity at low and high values of $\bar{X}$ are due for the formation of different structures and types of bonds in complexes of transition metal ions and phosphonic acid groups [13,14]. For example, for the ion-exchange resin KRF:







$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-[MeNO_3]^+$$

At the first portion of the curve of the dependence $\Delta H = f(\bar{X})$, corresponding to the small concentration of sorbed ions, transition metal ions can interact with two fixed groups. The increase in the energy of Co^{2+} and Cu^{2+} ions sorption at small values of $\bar{X}$ proves the same [8,9].

At the second portion of the curve where the additivity of immersion energies of H^+-form and metal forms of the ion-exchange resin is observed, the metal ion interacts with one fixed group of the resin. The find deviation from linearity as $\bar{X} \rightarrow 1$ can be explained by the presence of the ion couples of the

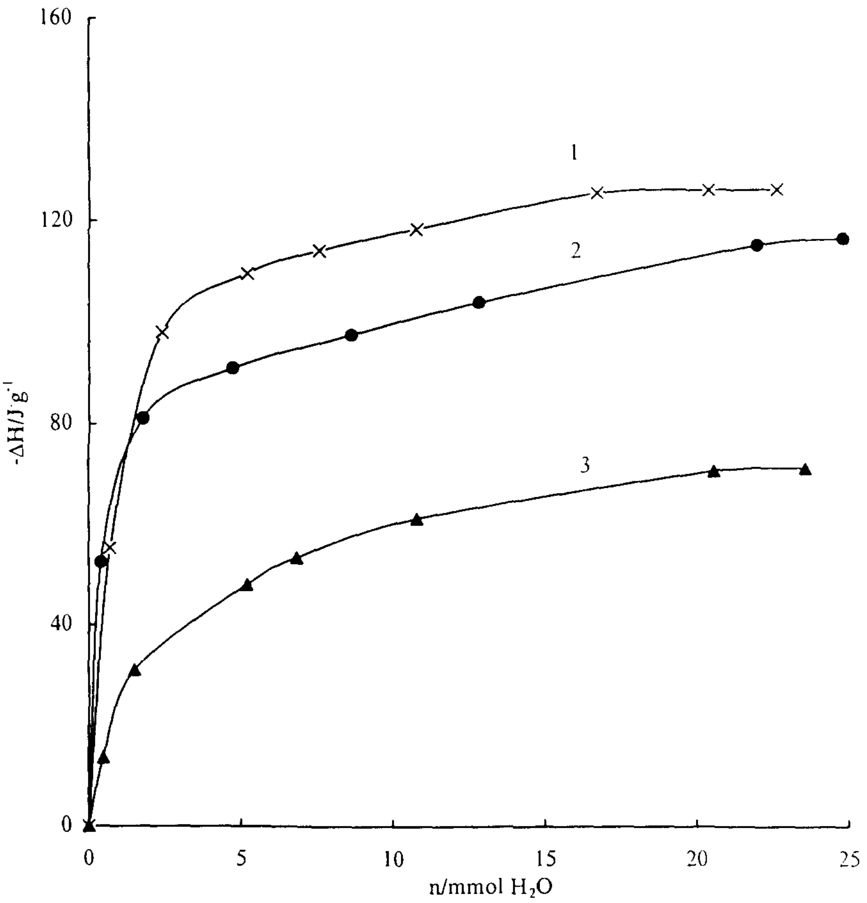


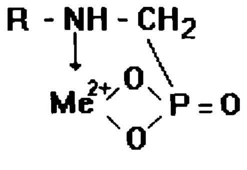
Fig. 3. Enthalpy of partial hydration (1) Cu^{2+}; (2) Co^{2+} and (3) H^{+} forms of KRF resins.

$MeNO_{3+}$ type in the resin phase at large metal concentrations.

The kind of the sorbed complex depends on the concentration of metal ions on the resins. If the structure of the complexes changes, then the interaction energy between water molecules and the metal-containing resin naturally also changes and the additive property of the hydrogen form and the metallic form of the resin hydration energy is not observed.

For the AMF and ADF ion-exchange resins the dissociation constant is larger than that of the KRF-5p ion-exchange resin. Their functional groups are ionized to a greater extent and form a stronger bond with water dipoles that increases the immersion energy.

The immersion energy of strong acidic sulphocationic exchanger is 169.9 J/g. Unlike the KRF-5p resin the immersion energies of Co^{2+} and Cu^{2+}-substituted AMF and ADF decrease with the increase of $\bar{X}$. This may be due to the tighter bonding between the metal ions and the functional groups of AMF and ADF resins. Transition metal ions and ligand groups of the ion-exchanger resins form the following chelate complexes [15]:



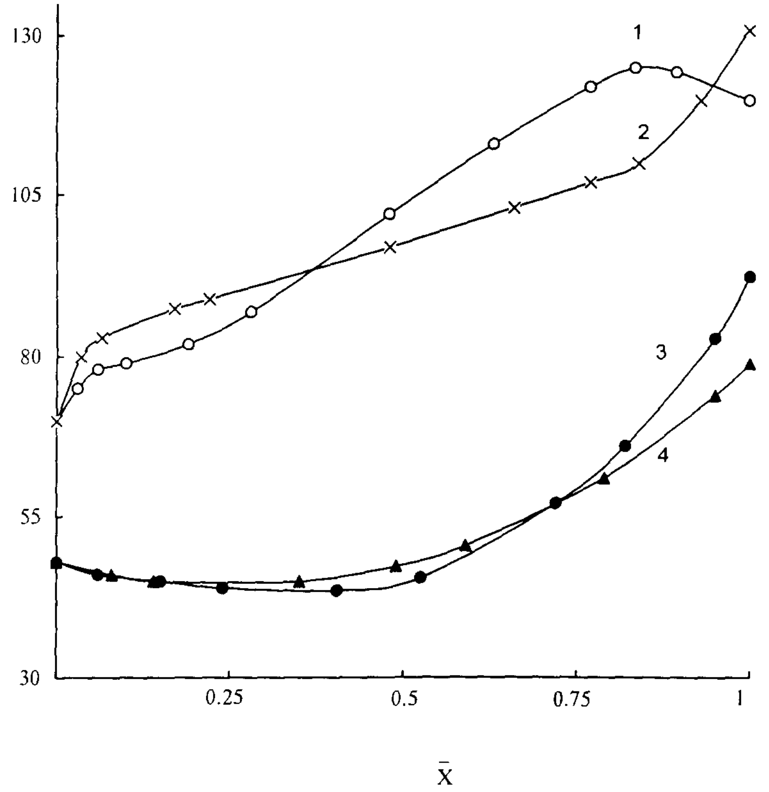
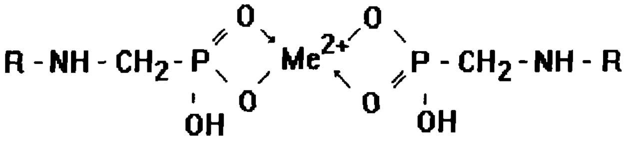
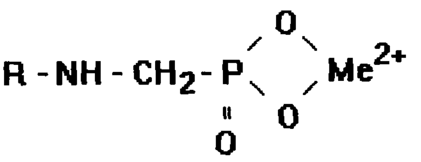


Fig. 4. (a) Dependencies of the immersion heats of the ion-exchange resins on the metal ions loads in KRF resin: (1) Co^{2+}; (2) Cu^{2+}, in AS resin: (3) Co^{2+}; (4) Cu^{2+}.(b) Dependencies of the immersion heats of the ion-exchange resins on the metal ions loads in ADF resin: (1) Co^{2+}; (2) Cu^{2+}, in AMF resin: (3) Co^{2+}; (4) Cu^{2+}.

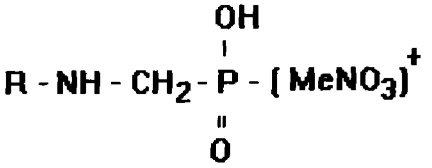
Complexes without amino groups may also be found



For large loads ionic bonds would result in



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



$$R-NH-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{P}}-[MeNO_3]^+$$

in which the ligands taking a large part in the inner coordination sphere of the ions reduce their hydration. The amino groups present increase the stability of the complex. As a result, the sorbed ions do not increase the immersion energy; moreover, they bind the ionized functional groups of the ion-exchange resins and prevent their hydration.

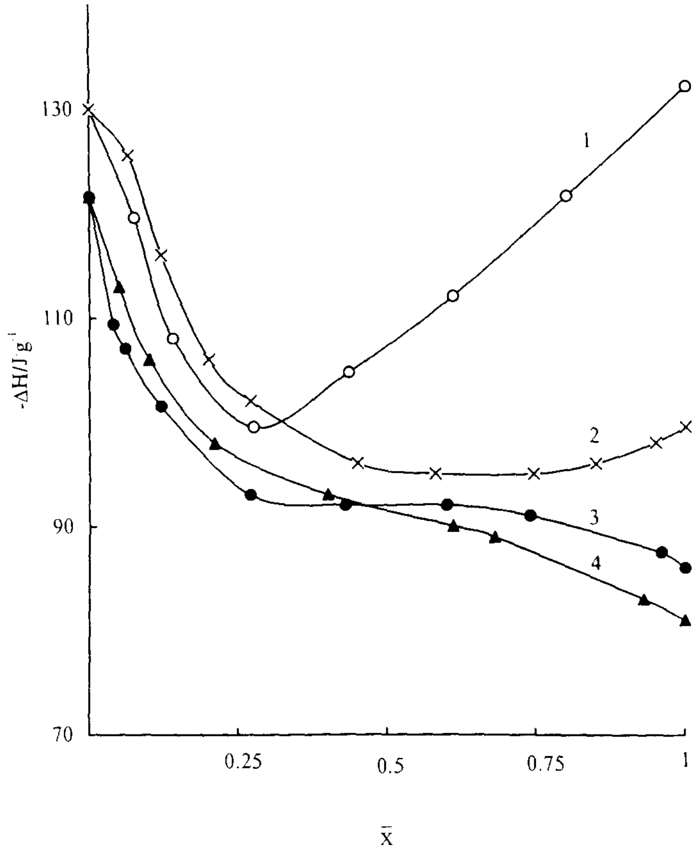


Fig. 4. (continued)

However, the increase in the metal ions content in the resin phase causes the increase of the immersion energy. The immersion energy of the AS ion-exchange resin up to $\bar{X} = 0.4$ changes insignificantly. The sorbed Co^{2+} ions are bound with several amino groups the concentration of which at small values of $\bar{X}$ considerably exceeds the concentration of Co^{2+} ions. The inner coordination sphere of Co^{2+} ions is saturated with amino groups. At higher values of $\bar{X}$ the immersion energy of the ion-exchange resin increases owing to water molecules entering the inner coordination sphere of metal ions. This is also true for the AMF and ADF ion-exchange resins.

The formation of different structures during the water interaction with resin is reflected on the dependence: hydration energy–metal content. This enables us to establish the intervals of the existence of certain complexes . Water makes the greatest contribution to energetic sorption processes. It is included into the coordinating sphere of metal ions and the monomolecular layer. The change of the hydration energy dependence on the metal concentration corresponds to the change of the catalytical activity of metal contained resins (Fig. 5).

The catalytic activity also correlates with the heat of the transition metal sorption [16]. The coordinating number of metal ions is realized most fully at low loads of resins ($\bar{X}$). It causes a sharp rise in the heat of the sorption at $\bar{X} \rightarrow 0$. These complexes are most active in the catalytic reactions. With the increasing of the heat of the sorption the catalytic activity of the corresponding sorbate complex (on Me^{2+} mol) becomes high. If we calculate W^0 on resin's gram then curve $W^0 = f(C_R)$ is maximum (Fig. 5).

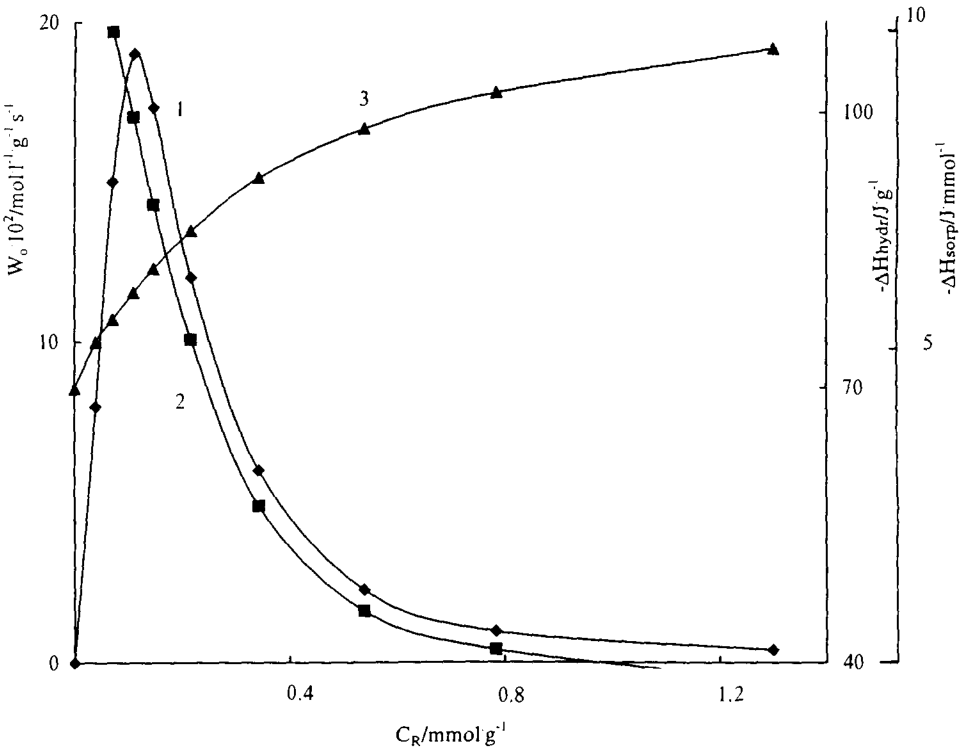


Fig. 5. Dependencies of beginning speed decomposition H_2O_2; (1) of ΔH sorption (2) of ΔH hydration (3) on the content of copper ions loads in the resin KRF.

References

[1] R. Hering, Chelatbildende Ionenaustauscher, Akademie-Verlag, Berlin, 1967.
[2] S.K. Sahni and J. Reedijk, Coord. Chem. Rev., 59 (1984) 1.
[3] V.D. Kopylova, J. Phys. Chem. (Russ.)., 63 (1989) 1153.
[4] V.D. Kopylova and A.N. Astanina, Ionic Complexes in Catalyse, Khimija, (Russ.), 1987.
[5] G. Dobrowolska, G. Muszynska and J. Porath, J. of Chrom., 541 (1991) 333.
[6] L. Anderson, E. Sulkowski and J. Porath, Bioseparation, 2 (1991) 15.
[7] V.S. Soldatov, Simple Ion-exchange Equilibriums (Russ.), Nauka i tekhnika, Minsk, 1972.
[8] S.N. Hajiev, S.V. Kertman and Yu.A. Leykin, Thermochim. Acta, 139 (1989) 327.
[9] S.V. Kertman, G.M. Kertman and Yu.A. Leykin, Thermochim. Acta., 256 (1995) 227.
[10] G.M. Kertman, S.V. Kertman // 12th IUPAC Conf. Chem. Thermodyn. [and] Jt Meet. 47th Calorim. Conf., Snowbird, UT, USA. 1992. p.370.
[11] G.A. Krestov, Thermodynamic Ionic Processes in Solution, Moscow Khimija, (Russ.), 1973.
[12] A. Marton, E. Kocsıs and J. Inczedy, Talanta, 30 (1983) 709.
[13] Yu.A. Leykin, S.U. Gladkov and E.A. Vilipov, Radiokhim. (Russ.), 5 (1979) 516.
[14] K.M. Saldadze and V.D. Kopylova-Valova, Complex-forming Resins, Moscow, Khimija (Russ.), 1980.
[15] S.K. Sahni, R. Bennecom and J. Reedijk, Polyhedron, 4 (1985) 1634.
[16] S.V. Kertman, G.M. Kertman and M.V. Tomilova, Kinetika i kataliz (Russ.), 34 (1993) 1035.