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THERMOCHEMICAL STUDY OF ION-EXCHANGE PROCESSES. V. SORPTION OF COPPER IONS IN COMPLEX-FORMING RESINS *,**

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ABSTRACT

The thermodynamic process of copper ion sorption from nitrate solutions has been studied in complex-forming nitrogen and phosphorus resins with the help of a Calvet microcalorimeter. Direct calorimetric measurements were performed at different extents of exchange and the enthalpy variations for the system were obtained. The experimental results show that the van't Hoff equation cannot be used for calculating the enthalpy sorption of transition metal ions in the complex-forming resins.

INTRODUCTION

The theory of simple ion-exchange processes is well developed [1], but for compounds such as complex-forming resins work has started only recently. As a matter of fact, the formation of coordinating bonds is an extra complicating factor in the resins. To develop the theory one should know thermodynamic values, especially the ion-exchange enthalpy. The enthalpy change for the ion-exchange process for heterogeneous systems is often obtained from the temperature dependence of the equilibrium constants using the equation of van't Hoff [2], though the equation is generally used for homogeneous reactions. The reliability of the results for the ion-exchange process for heterogeneous reactions calculated from the equation of van't Hoff should be tested by comparison with the experimental data of calorimetric measurements. Good agreement between the calculated and experimental data is observed only in the cases of the ion-exchange of alkali and alkaline earth metals [3–5]. Direct calorimetric measurement is the best way to obtain reliable values of the ion-exchange enthalpy [6].

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* Dedicated to Professor E.F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.
** For part IV see J. Phys. Chem., 61 (1987) 1426 (in Russian).

EXPERIMENTAL

Reagents

The resins used were synthesized from a base copolymer of styrene and divinylbenzene. Resin functional groups are given in Table 1. The sorption of copper ions was performed from copper nitrate.

The value of the sorption enthalpy greatly depends on the nature of the anions [7,8]. The nitrate ion is a poor ligand and contributes little to the total enthalpy value. Enthalpies of ion-exchange were measured using a Calvet differential microcalorimeter MID-200.

A previously moistened resin sample of 0.2 g was placed into the calorimeter and, after thermostatting, was brought into contact with a thermostatted solution of copper 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 dissolution 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 values in ref. 9. The initial and equilibrium concentrations of copper ions were determined using an AAS-1 atomic absorption spectrometer.

RESULTS AND DISCUSSION

The enthalpy ΔH and the equilibrium constant of ion-exchange K are known to depend on the filling phase $\overline{X}$ of the resin sorbed by the ions [3,7,10–14]. Therefore, when calculating ΔH from $\lg K$ vs. $1/T$, $\overline{X}$ should be fixed. The value of ΔH for sorption of copper ions in ADF was -0.8 J mol^{-1} at $\overline{X} = 0.49$ (obtained calorimetrically) and -37 kJ mol^{-1} (calculated from the equation of van't Hoff). For copper ion sorption in the resin AMF the calculated ΔH is $+26$ kJ mol^{-1} at $\overline{X} = 0.6$ and the experimental ΔH is -5.6 kJ mol^{-1}, i.e. they even differ in sign. This difference is obviously

TABLE 1

Resins studied

Resin	Functional group
KRF	R–$PO(OH)_2$
SDF-1	R–PO(OH)–CH_2–$PO(OH)_2$
SDF-2	R–PO(OH)–CH_2–CH_2–$PO(OH)_2$
AS	R–NH_2
AMF	R–NH–CH_2–$PO(OH)_2$
ADF	R–NH–CH_2–$PO(OH)_2$; R–$PO(OH)_2$

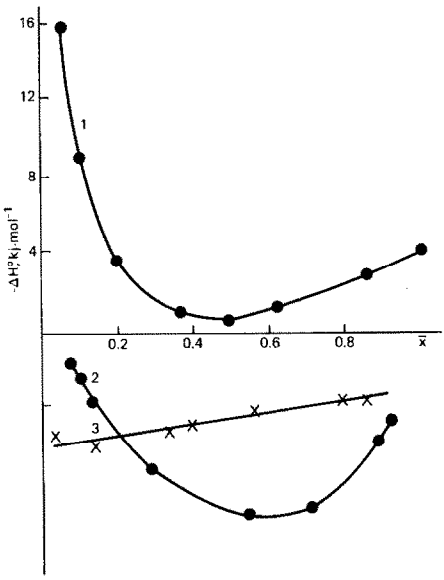


Fig. 1. Enthalpies of partial exchange of copper ions in ADF resin. 1, 298 K; 2, 313 K; 3, 333 K.

caused by the fact that the resin sorbs hydrated ions [6], and the degree of hydration of the latter varies considerably at different temperatures. Moreover, the change in the temperature affects the constant of deprotonation of resin functional groups. Figure 1 shows the effect of temperature on the

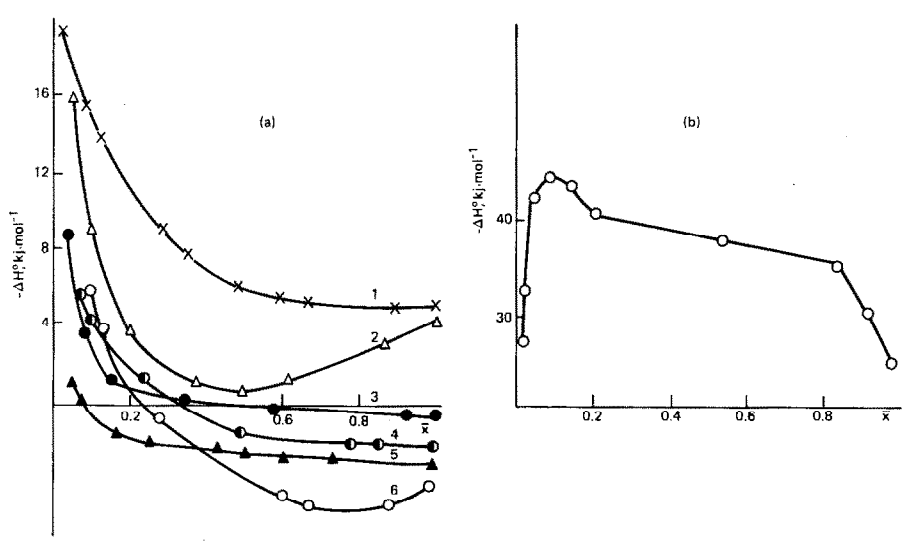


Fig. 2. Standard enthalpies of partial exchange of copper ions in resins. (a) 1, AMF; 2, ADF; 3, KRF-5p; 4, SDF-1; 5, KRF-2p; 6, SDF-2. (b) AS.

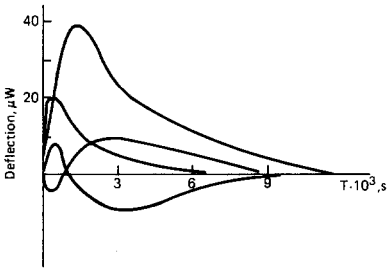


Fig. 3. Experimental calorimeter curve. Resin/concentration of copper ion: 1, AS/0.01 M; 2, AS/0.002 M; 3, AMF/0.002 M; 4, KRF-5p/0.005 M.

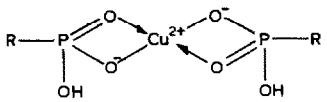
enthalpy of copper sorption in the resin ADF. At $T = 313$ K, and especially at $T = 333$ K, the sorption process is endothermic, whereas at $T = 298$ K it is exothermic over the whole $\overline{X}$ range. This proves that ion-exchange considerably affects the enthalpy of the initial and final states.

It is thus evident that calculating ΔH of ion-exchange using the equation may cause inadmissibly erroneous results, especially in the case of transition metal ion sorption in complex-forming resins. When copper ions are sorbed in phosphorus-containing cationites with an increase in the degree of filling of the resin phase, both the value and the sign of the sorption enthalpy change (Fig. 2). This may be explained by the synchronous influence of the following factors: the deformation of the three-dimensional hydrocarbon resin frame; the dehydration of copper ions during the change into the resin phase; the increase of ion exchange and the decrease of the coordinating interaction between the sorbed copper ions and resin functional groups [15]. The pK values determined by potentiometric titration using the modified Henderson–Hasselbah equation are -2.81 for KRF-2p and -3.11 for KRF-5p. Phosphate groups in KRF-2p thus dissociate to a greater extent, which causes the sorption process to be more endothermic.

It is evident from the thermokinetic curve (Fig. 3) that copper ion sorption in the phosphate cationites proceeds with a short high-speed exo effect caused by copper-complex formation with the fixed resin groups, followed by a longer period with an endo effect. When solutions having larger coppper ion concentrations are sorbed, the exo effect is not observed. This proves that, at a high concentration of copper, ionic bonding predominates over the coordination.

It has been reported [9] that the sorption of cobalt ions in the resin KRF-5p is exothermic over the whole range of resin-filling phases. This may be connected with the fact that for cobalt ions a coordinating interaction with phosphate groups is much more common than for copper ions. A larger effective concentration of copper ions in comparison with cobalt ions increases ion-interaction with the resin functional groups when copper ions are sorbed. If, in monofunctional phosphoric resins, complex formation of

copper ions with two phosphoric groups (1) affects the conformation of the polymeric matrix chain, then in the complex-forming phase of diphosphoric reisins (2) the conformation changes become smaller [16].



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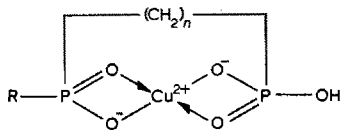

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Therefore, sorption in diphosphoric resins could be expected to be more exothermic because of a decrease in the energy lost through conformation changes. An energy gain with copper ion sorption, however, is not observed. This can be explained by dehydration processes. The water molecules are displaced from the first coordination sphere of copper ions when a complex is formed with a resin functional group. The presence of CH_2 groups bonding phosphorus atoms in SDF resins enlarges the space occupied by ligand groups in the coordination sphere of metal ions and provides much fuller dehydration in comparison with KRF resins.

The resins AMF and ADF, except those having phosphonic groups, contain secondary amino groups which considerably influence the sorption enthalpy. The presence of amino groups intensifies the coordinating interaction between the copper ions and the resins. Therefore, the sorption process over the whole $\overline{X}$ range proceeds exothermically with a large energy release. The formation of Cu^{2+}–N bonds is energetically more preferable than the formation of Cu^{2+}–O bonds [17]. The maximum energy gain is observed both with sorption in phosphoric resins and, hence, at small concentrations of copper ions in solution in the resin phase. It is controlled on the one hand by attainment of the full copper coordinating number, and on the other hand by the minimum energy spent on deformation of the polymeric resin matrix. At small copper concentrations in the resin there is a sufficient number of ligand groups existing in the conformation required for complex formation. With an increase in the copper ion content in the process of complex formation the ligand groups which gain the least energy are involved. The enthalpy of copper ion sorption in the nitric resins AS has negative values over the whole $\overline{X}$ range (Fig. 2b).

For aminostyrene a steep drop in the energy released is observed at $\overline{X} \rightarrow O$, which has been reported in the literature [18,19]. There, when defining the enthalpy of copper ion complex formation with poly-

aminostyrene there was a marked drop in the absolute value of ΔH where the number of coordinating bonds between copper and amino groups increased. It is interesting to note that there is a small endo effect at the initial stage of copper ion sorption in AS (Fig. 3) which is not observed in the resins AMF and ADF. To explain the ion exchange processes, especially accompanied by complex formation, one should separately determine the energy contribution of the separate terms: the enthalpy of the coordinating bonds of the metal and resin ligand groups, the enthalpy of the dehydration of resin ligand groups, the enthalpy of the water displacement from the first coordination sphere of the metal and the enthalpy of the deformation of the resin polymer matrix. This work is planned for the future.

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