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THERMODYNAMICS OF ION EXCHANGE IN A SULFONATED POLYMER BASED ON *cis*-TETRAPHENYLMETACYCLOPHANOCTOL

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The thermodynamic characteristics of proton exchange in SO_3H groups of a sulfonated network polymer based on *cis*-tetraphenylmetacyclophanoctol for Na^+, Cu^{2+} cations from aqueous solutions were considered for the first time. Microcalorimetric measurements of the heat effects of Na^+–H^+ and Cu^{2+}–H^+ exchanges were performed, equilibrium compositions of polymer and solution were determined. The changes of Gibbs energy, enthalpy and entropy of ion exchange were calculated.

Keywords: *ion exchange, microcalorimetry, sulfonated polytetraphenylmetacyclophanoctol, thermodynamic functions*

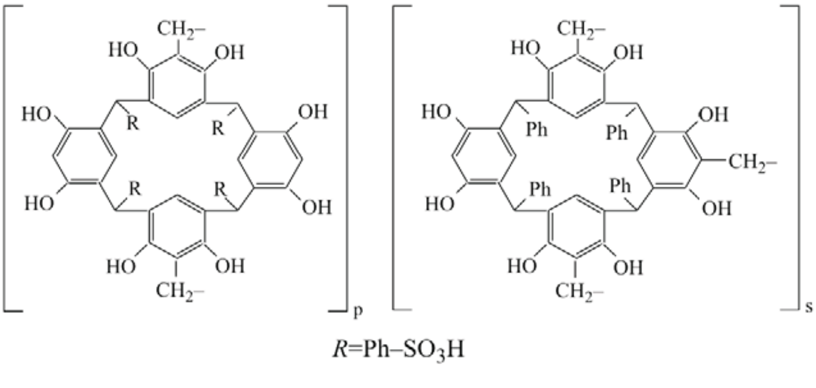
Introduction

Owing to their unique structure which includes a large internal cavity and hydrophilic loop comprising eight hydroxyl groups, *cis*-metacyclophanoctols attract considerable attention of nanochemistry and supramolecular chemistry [1]. It is known, that *cis*-metacyclophanoctols immobilized in a polymeric phase form assemblies with participation of alkaline [2, 3], transitive [4, 5] metal cations and ammonium [6] cations, are nanoreactors for catalytic hydrogenation processes [7, 8], on their basis polyelectrolytes [9] and the polymer composites containing metal nanoparticles of the adjustable size [7] are received.

We have synthesized the network polymers containing immobilized metacyclophanoctols [2]. It is established, that these polymers are weakly acidic cation exchangers [10]. The functionalization of immobilized metacyclophanoctols via incorporation of ionogen carboxyl [4], furylhydroxymethyl [11] or phosphonate [5] groups result in the increase of interaction selectivity of polymers with cations. For example, the introduction of (2-furyl)-hydroxymethyl groups into the structure of the *cis*-metacyclophanoctol base unit of the polymer decreases the enthalpy of sorption of ammonium cations and increases the enthalpy of sorption of sodium cations and raises the affinity of polymer to ammonium cations [12].

We synthesized the new network polymer containing sulfonated *cis*-tetraphenylmetacyclophanoctol in the repeating unit [13].

Owing to the presence of weakly acidic hydroxyl and strongly acidic SO_3H groups this polymer shows cation exchanger properties in a wide range of pH, has a high ion exchanger capacity [14]. The structure of repeating unit of sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol causes more organized arrangement of SO_3H groups in it as against commercial cationites. It can result in the increase of affinity of the synthesized polymer to metal cations



R=Ph–SO_3H

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and be reflected in value of thermodynamic functions of reversible process of cation exchange

$$z\overline{\mathrm{H}}^{+}+\mathrm{Cat}^{z+}\leftrightarrows\overline{\mathrm{Cat}}^{z+}+z\mathrm{H}^{+} \qquad (1)$$

where overbars label polymeric phase constituents.

The purpose of this work was to study the thermodynamic characteristics of the protons exchange of high-acidity SO_3H groups of a sulfonated network polymer based on *cis*-tetraphenylmetacyclophanoctol by reaction (1). To solve the problem formulated above, we measured the heat effects and determined the equilibrium compositions of the polymer and solution phases involved in processes (1) at $\mathrm{Cat}^{z+}=\mathrm{Na}^{+}$, Cu^{2+}.

Experimental

The polymer was prepared by twice sulfonating of the network polymer synthesized by the resol polycondensation of *cis*-tetraphenylmetacyclophanoctol with formaldehyde following the procedure described in [2]. The total ion-exchange capacity of the sulfonated polymer with respect to 0.1 M NaOH was 5.65 equivalents per kg dry polymer. Of these, 2.45 equivalents correspond to the exchangeable SO_3H protons.

Solutions were prepared using HCl and NaCl of chemically pure grade and $CuCl_2\cdot 2H_2O$ of pure grade. The amount of cations sorbed and desorbed in ion exchange was calculated from changes in ion concentrations in solution. The concentration of H^+ was determined by acid-base titration with methyl red as an indicator. Cu^{2+} was determined by complexonometric titration, the indicator was 1-(2-pyridylazo)-2-naphthol [15].

The heat effects of ion exchange were measured at 293 K on a DAK-1-1A microcalorimeter under isothermal conditions with automatically balancing thermal EMF at the expense of the Peltier effect. The sensitivity of the calorimeter was 0.04 V W^{-1}. The microcalorimeter was calibrated by dissolving chemically pure cesium chloride in water; the reference value used in calculations was $\Delta_{\mathrm{aq}}H^{0}_{\mathrm{CsCl}}=$ 17205±5 J mol^{-1} [16]. Measurements were performed in standard (control and measuring) stainless steel ampules of volume 6 mL. An accurately weighed amount of swollen ionite was immersed into an aqueous solution of an electrolyte (5.3 mL, measuring ampule) and water (5.3 mL, control ampule) to determine the difference of the corresponding heat effects. The mass of the swollen polymer was 0.0100–0.0300 g. The polymer in the H form was immersed into 0.001–0.005 M solutions of $CuCl_2$ or 0.01–0.1 M solutions of NaCl, and the polymer in the salt form, into 0.001–0.006 M solutions of HCl. The heat flux was 10^{-5}–10^{-4} W.

The equilibrium distribution metal cations in the system of electrolyte solution – polymer was studied by the dynamic method [17]. The polymer in the salt or H form was placed into a column, through which aqueous solutions containing two electrolytes, HCl and NaCl or HCl and $CuCl_2$, were passed until the column was equilibrated at 293 K. Equilibrium was considered to be established when the concentrations of electrolytes in the initial solution and several sequentially taken filtrate samples coincided. The equilibrium ion composition of the polymer phase was independent of the initial polymer form. Taking [18] into account, the differential Gibbs energy of proton exchange in polymer for metal cations from aqueous solutions was calculated from the experimental data on equilibrium solution and polymer compositions as $\Delta\overline{G}=RT[(z_{\mathrm{Cat}}-z_{\mathrm{H}})-\ln k^{\mathrm{a}}_{\mathrm{Cat/H}}]$. Here z_{i} is cation charge; $k^{\mathrm{a}}_{\mathrm{Cat/H}}$ is the corrected ion exchange selectivity coefficient [19] calculated as

$$k^{\mathrm{a}}_{\mathrm{Cat/H}}=\frac{x_{\mathrm{Cat}}}{x^{z}_{\mathrm{H}}}\frac{m^{z}_{\mathrm{H}}}{m_{\mathrm{Cat}}}\frac{\gamma^{2z}_{\pm\mathrm{HCl}}}{\gamma^{(z+1)}_{\pm\mathrm{CatCl}_z}}$$

where x_{i} is the equivalent cation fraction in the polymer; m_{i} is the cation molality in solution; and $\gamma_{\pm}$ is the mean ionic molal activity coefficient of the electrolyte in aqueous solution. The mean ionic molal activity coefficients of $CuCl_2$ in solutions were calculated by the Debye–Huckel equation on the assumption that the closest approach distance of ions was 4.5 Å [20].

Results and discussion

Energy of interaction of ions with repeating unit of polymer, solvation energy of ions in a solution and polymer are the factors determining selectivity of interaction of ionite with aqueous solutions of electrolytes on Eq. (1) [21]. The character of the dependence of differential thermodynamic functions of process (1) from the content of metal cations in polymer can reflect features of interaction of exchanging ions with ionogen groups. Differential thermodynamic functions of cation exchange in a sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol on reaction (1) are shown in Figs 1–3.

Value of differential change of Gibbs energy of an ionic exchange depends on nature of sorbed cation and counterion content of a polymeric phase (Fig. 1). The dependence of $\Delta\overline{G}_{\mathrm{Cat/H}}$ on x_{Cat} for singly charged Na^+ cations is described by the equation $\Delta\overline{G}_{\mathrm{Na/H}}=6.63x_{\mathrm{Na}}-2.18$ (the linear correlation coefficient is 0.95). The linear kind of function is defined by change of electrostatic (coulombic) interactions of exchanging sodium cation and a proton with the anions of polymer functional groups and absence of ad-

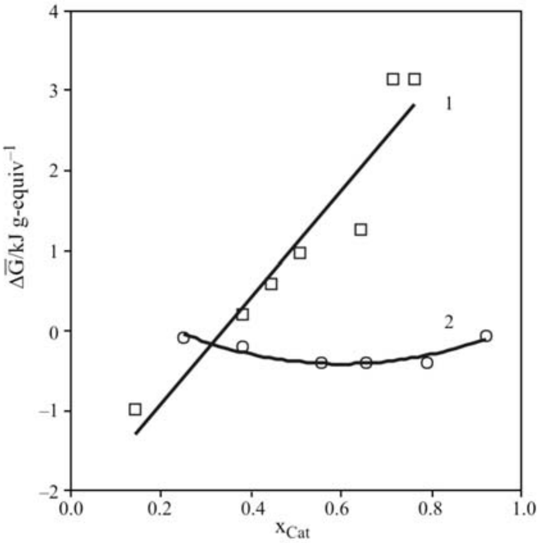

Fig. 1 Differential Gibbs energy of exchange for the 1 – Na^+–H^+, 2 – Cu^{2+}–H^+ reactions in the sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol at 293 K

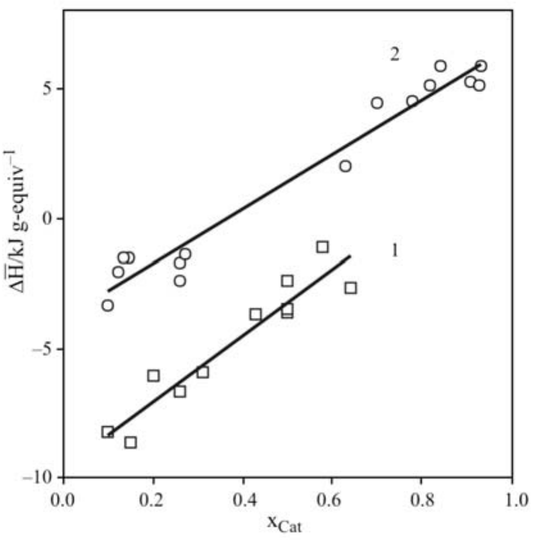

Fig. 2 Differential enthalpy of exchange for the 1 – Na^+–H^+, 2 – Cu^{2+}–H^+ reactions in the sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol at 293 K

ditional (non coulombic) interactions. Increase in $\Delta\bar{G}_{Na/H}$ as concentration sodium cation in a polymeric phase increases is determined by the well-known energy nonequivalence of exchange sites [21]. For doubly charged Cu^{2+} cations dependence $\Delta\bar{G}(x_{Cat/H})$ is non-linear and has a maximum at x_{Cu}=0.6. Probably, copper cations participate in formation of supramolecular assemblies in a polymeric phase alongside with electrostatic interactions.

The differential enthalpies of proton exchange for sodium and copper cations, $\Delta H=(\partial\Delta H/\partial x_{Cat})_T$, are shown in Fig. 2. $\Delta\bar{H}$ values correspond to x_{Cat} at the middle of the interval of changes in the counterion polymer composition during measurements of the heat effect of ion exchange. $\Delta\bar{H}(x_{Cat})$ dependences are rectilinear (the linear correlation coefficients of $\Delta\bar{H}(x_{Na})$ and $\Delta\bar{H}(x_{Cu})$ functions are 0.95 and 0.98, respectively). An increase in the differential enthalpy of ion exchange as the content of metal cations in the polymer grows is determined by the energy non-equivalence of exchange sites in the polymer.

The differential entropies of ion exchange, $\Delta\bar{S}$, calculated by the equation

$$(\Delta\bar{S})_{T,x_{Cat}}=\left(\frac{\Delta\bar{H}-\Delta\bar{G}}{T}\right)_{T,x_{Cat}}$$

are shown in Fig. 3. The dependence of entropy change from concentration of metal cations in polymer at exchange Na^+–H^+ is rectilinear, and at exchange Cu^{2+}–H^+ is square-law. The entropy of the system increases as the fraction of metal cations in the polymer grows for both Na^+–H^+ and Cu^{2+}–H^+ exchange processes. This is in agreement with the results of semiempiric quantum-chemical calculations of assemblies of the *cis*-tetraphenylmetacyclophanoctol anion with the H_3O^+, Na^+ cations. These assemblies model the structure of the polymer repeating unit in the H and Na forms. Calculations show that the replacement of hydroxonium cations with Na^+ or $Na^+\cdot H_2O$ cations causes the structure loosening. Thus, the dependences of the differential thermodynamic functions of ion exchange on the counterion polymer composition are determined by changes in the interaction between the exchanging ions and ionogen groups.

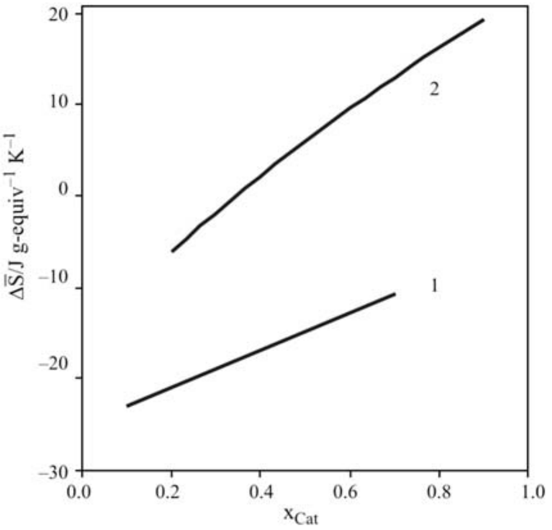

Fig. 3 Differential entropy of exchange for the 1 – Na^+–H^+, 2 – Cu^{2+}–H^+ reactions in the sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol at 293 K

Standard thermodynamic functions of exchange sulfonated network polymer based on *cis*-tetraphenylmetacyclophanoctol for metal cations from aqueous solutions (table) are obtained by the integration of

Table 1 Standard thermodynamic functions of cation exchange in sulfonated network polymer based on *cis*-tetraphenylmetacyclophanoctol (reaction (1)) at 293 K

Cat	ΔG^0/ kJ g-equiv^{-1}	ΔH^0/ kJ g-equiv^{-1}	ΔS^0/ J g-equiv^{-1} K^{-1}
Na^+	1.1±0.1	–3.2±0.7	–14.7
Cu^{2+}	–0.1±0.1	1.4±0.7	5.97

corresponding differential functions with respect to the composition of polymer between limits $x_{Cat}=0$ and to $x_{Cat}=1$. For example, the integral enthalpies of ion exchange calculated by the equation

$$\Delta H = \int_0^1 (\partial \Delta H / \partial x_{Cat})\mathrm{d}x_{Cat}$$

The obtained ΔH values are the standard enthalpies of ion exchange because the heats of mixing and the difference in heat content between 0.1 M solutions of NaCl and HCl or 0.005 M solutions of $CuCl_2$ and HCl are smaller than measurement errors.

The standard thermodynamic functions of ion exchange are strongly influenced by the difference in the resolvation energies of the ions involved in exchange [21]. The table shows that the affinity of investigated polymer (decrease of ΔG^0 values) for cations increases in sequence Na^+, H^+, Cu^{2+}. Change of free energy and a direction of processes of exchange Na^+–H^+ and Cu^{2+}–H^+ is defined by increase of entropy in the polymer-solution system. The enthalpy and entropy of system increase when protons of SO_3H groups of a sulfonated polymer based on *cis*-tetraphenylmetacyclophanoctol are exchanged by Cu^{2+} cations from aqueous solutions. Probably, the last is caused with significant expenses of energy on dehydration of doubly charged cations.

Conclusions

Microcalorimetric measurements of the heat effects and definitions of equilibrium compositions of polymer and solution have allowed to calculate the thermodynamic functions of processes of Na^+–H^+ and Cu^{2+}–H^+ exchange in sulfonated network polymer based on *cis*-tetraphenylmetacyclophanoctol. It is revealed, that polymer shows relatively greater affinity to copper cations comparatively with singly charged Na^+ and H^+ cations. Comparison of thermodynamic functions shows, that the sign of Gibbs energy change and character of $\Delta\overline{G}_{Cat/H}(x_{Cat})$ dependence is defined by entropy component as for sorption of copper cation, and sodium cation. Rectilinear dependence of differential thermodynamic functions ($\Delta\overline{G}_{Na/H}$, $\Delta\overline{H}_{Na/H}$, $\Delta\overline{S}_{Na/H}$) from the sodium contents in polymer argues for presence of the same electrostatic interactions of exchanging cations with anions of polymer functional groups, energy nonequivalence of exchange sites and the absence of additional (non coulombic) interactions in a polymeric phase at Na^+–H^+ exchange. Non-linearity of functions $\Delta\overline{G}_{Cu/H}(x_{Cu})$ and $\Delta\overline{S}_{Cu/H}(x_{Cu})$ reflects the presence of non coulombic interactions with participation copper cations in a polymeric phase.

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