

Hydration of ion exchangers: Thermodynamics and quantum chemistry calculations [☆]

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ABSTRACT

Comparative studies of the state of water molecules in carboxylic acid resins were carried out using classic thermodynamics and *ab initio* quantum chemical calculation of the structure of representative fragments of their polymeric matrix in the presence of different amounts of water molecules. Water sorption isotherms were obtained for H⁺, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Ba²⁺ forms of the carboxylic acid ion exchanger Lewatit S8227 using the isopiestic method. Quantum chemistry calculations were performed by the Firefly QC package, which is partially based on the GAMESS (US) source code, on the theory level RHF/MINI. Atomic structures of fragments of the resin interior containing 1–6 monomeric residues and 0–10 water molecules per functional group were computed. It has been shown that the water sorption isotherms are well described by the previously derived equation on the assumption of the presence in the swollen ion exchanger of one or two formal hydrates. Quantum chemistry calculations allow independent evaluation of the number of water molecules in the hydrates and in so doing reduce the number of fitting parameters needed for quantitative description of the water sorption isotherms. They also allow classifying the water molecules in the resin according to the type of interaction with fixed ion-counter-ion ion pair.

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1. Introduction

The sorption properties of ion exchangers depend on the mutual interaction of three main constituents of the resin phase which are: functional group, counter-ions and water molecules. This interaction is unseparable into a simple sum of the pair interactions. Therefore the hydration of ion exchangers may not be considered without accounting for the interionic interaction.

Thermodynamic functions of water sorption by ion exchangers, calculated from the water sorption isotherms and thermochemical measurements are the most reliable fundamental characteristics of the hydration process but they do not give direct information of intermolecular interactions and the structure of hydrates. Existing models interpreting macroscopic properties on the atomic level leave too much freedom for speculation and do not allow defining the structure of the hydration complexes. In contrast, computer modelling of representative fragments of ion exchangers and quan-

tum chemical calculation gives concrete parameters of the molecular structure of fragment containing several functional groups, counter-ions and water molecules, such as: distances between atoms, length of bonds, energy of pair interactions and degree of covalence of the bond. At the same time calculation of macroscopic properties of the whole system from the properties of the microstate at present is practically impossible. Thus thermodynamic and quantum chemistry approaches to the description of the hydration of ion exchangers are complementary and their joint application is promising for a more accurate interpretation of hydration and intermolecular interactions in ion exchangers. Existing literature data do not allow that. Literature data on the thermodynamics of water sorption by carboxylic acid resins are scarce. The only systematic data on this matter were obtained on the copolymer of methacrylic acid and divinylbenzene for alkali and alkali earth ionic forms [1]. Computer modelling of carboxylic acid resins was recently described [2], and Nechaeva et al. [3] attempted to model a separate molecule of the sodium salt of pivalic acid.

In this paper new results on thermodynamic studies of water sorption by carboxylic acid ion exchangers, exemplified Lewatit S8227, are compared with structural and energy characteristics of its hydrated fragments.

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2. Experimental

All chemicals used in the experiments were of analytical grade. The carboxylic acid ion exchanger Lewatit S8227, a porous resin on the basis of a cross-linked polyacrylic acid, was used for the isopiestic experiments on water sorption. Its full capacity and water uptake in the hydrogen form was 12.0 meq g^{-1} and $1.07 \text{ g}_{\text{H}_2\text{O}} \text{ g}^{-1}$ respectively. The monoionic forms contained not less than 98% of the target counter-ion. Water sorption isotherms were obtained for the H^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} forms of the resin using the isopiestic method.

Samples of the ion exchanger $\sim 0.5 \text{ g}$ weight with precision $\pm 0.2 \text{ mg}$ in weighing bottles were placed in sealed plastic vessels kept in the thermostat as temperature $25 \pm 0.2 \text{ }^\circ\text{C}$ over saturated solutions of salts or sulfuric acid with known relative humidity, $\alpha = P/P_0$, of the equilibrium water vapour: (0.10 – 65% H_2SO_4 ; 0.20 – 58% H_2SO_4 ; 0.35 – CaCl_2 ; 0.45 – K_2CO_3 ; 0.53 – $\text{Mg}(\text{NO}_3)_2$; 0.65 – NaNO_2 ; 0.75 – NaCl ; 0.80 – $(\text{NH}_4)_2\text{SO}_4$; 0.84 – KCl ; 0.92 – Na_2CO_3 ; 0.97–10% H_2SO_4) [4], (Table 1) till constant weight reached (up to 30 days). Then the samples were dried at $105 \text{ }^\circ\text{C}$ and the water sorption was calculated from the weights of dry and wet samples. Water uptake from liquid water was determined using a centrifugation method.

Ab initio quantum chemistry calculations were performed by the Firefly QC package [5], which is partially based on the GAMESS (US) source code [6], on the theory level RHF/MINI [7]. Coordinates of all atoms were optimized to the achievement of minimum of the full energy of the system. Atomic structures of fragments of the resin interior containing 1–6 monomeric residues and 0–10 water molecules per functional group were computed. In some cases the structure of fragments contained up to 18 functional groups.

3. Results and discussion

3.1. Water sorption

Experimental results are presented in Table 1.

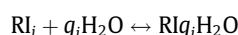
Two issues immediately follow from the experimental data on water sorption presented in Table 1. The water uptake from liquid and gas phases at $P/P_0 = 1$ are different. This phenomenon, known as Shroeder effect [8], in our specific case can be qualitatively explained by the porous structure of Lewatit S8227. Filling of perma-

nent pores with liquid water from saturated vapour is slow because it proceeds under a small difference of the chemical potential of water in the bulk and pores. Because of this the true equilibrium between water vapour and the porous resin is not reached during the experimental observation time. It seems that in our specific case this effect is mainly due to presence of macroscopic pores whose volume is equal approximately 0.5 cm^3 per gram of matrix and slightly affected by the nature of the counter-ion (see the bottom line in Table 1). Recent data [9] on careful direct measurements of the water uptake from water vapour and liquid water show that the same effect is observed for gel type resins of a different nature. It is most probable that it is caused by the uncontrolled inclusion of macroscopic cavities or defects in the polymer body.

This means that the water uptake from the liquid phase is poor characteristics of ion exchange resins, especially those with low cross-linkage.

The second feature of the carboxylic acid cation exchanger is the absence of correlation, or very weak correlation between hydration of the counter-ions and water uptake as observed earlier [1]. The data on water sorption were treated using the theoretical approach described [10] which allowed the derivation of a theoretical equation for water sorption isotherm $W = f(P/P_0)$. The main principles of this approach are as follows:

The water in the resin phase can be grouped into free molecules (bound only with other water molecules) and those bound into ionic hydrates (bound to the functional group or the counter ion, see Table 4). The hydrates are characterized by their formation constants



$$K_i = [\text{RI}q_i \text{H}_2\text{O}] / ([\text{RI}] \cdot \alpha^{q_i}) \quad (1)$$

The ion exchanger in equilibrium with water vapour is described as a mixture of hydrates and free water molecules.

The following equation for the water sorption isotherm was derived from these statements:

$$W = \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}} + \frac{\alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i}) \cdot f_W}{1 + W_0 - \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}} - \alpha \cdot (W_0 - \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}})} \quad (2)$$

Table 1
Water sorption^a by different ionic forms of resin Lewatit S8227 as a function relative humidity of water vapour.

P/P_0	H^+	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
0.10	0.048 (0.21)	0.228 (1.12)	0.171 (0.98)	0.139 (0.94)	0.309 (1.84)	0.174 (1.12)	0.121 (0.93)
0.20	0.064 (0.31)	0.295 (1.45)	0.241 (1.38)	0.195 (1.32)	0.385 (2.29)	0.230 (1.45)	0.151 (1.17)
0.35	0.082 (0.41)	0.350 (1.72)	0.319 (1.83)	0.332 (2.25)	0.438 (2.61)	0.277 (1.75)	0.188 (1.45)
0.45	0.0935 (0.43)	0.364 (1.79)	0.372 (2.13)	0.379 (2.57)	0.452 (2.70)	0.288 (1.82)	0.225 (1.73)
0.53	0.104 (0.48)	0.417 (2.05)	0.530 (3.03)	0.458 (3.10)	0.473 (2.82)	0.307 (1.94)	0.216 (1.67)
0.65	0.126 (0.58)	0.648 (3.19)	0.689 (3.95)	0.599 (4.06)	0.496 (2.96)	0.327 (2.06)	0.231 (1.78)
0.75	0.196 (0.91)	0.884 (4.35)	0.840 (4.81)	0.699 (4.74)	0.601 (3.59)	0.351 (2.21)	0.252 (1.94)
0.80	0.238 (1.10)	0.992 (4.88)	0.919 (5.26)	0.734 (4.97)	0.662 (3.95)	0.369 (2.33)	0.255 (1.97)
0.84	0.270 (1.25)	1.059 (5.21)	0.980 (5.62)	0.809 (5.48)	0.720 (4.30)	0.378 (2.39)	0.267 (2.06)
0.92	0.284 (1.65)	1.198 (5.89)	1.070 (6.13)	0.882 (5.97)	0.821 (4.91)	0.399 (2.52)	0.289 (2.23)
0.97	0.459 (2.13)	1.347 (6.62)	1.200 (6.87)	0.991 (6.71)	0.952 (5.69)	0.432 (2.72)	0.308 (2.37)
1.00 ^b	0.540 (2.50)	1.444 (7.10)	1.222 (7.00)	1.063 (7.20)	1.038 (6.20)	0.444 (2.80)	0.306 (2.35)
1.00 ^c	1.058 (4.90)	1.973 (9.70)	1.659 (9.50)	1.358 (9.20)	1.456 (8.70)	0.871 (5.50)	0.583 (4.50)
1.00 ^c –1.00 ^b	0.518 (2.40)	0.529 (2.60)	0.437 (2.50)	0.295 (2.00)	0.428 (2.50)	0.427 (2.70)	0.277 (2.15)
Δg matrix ^d	0.518	0.574	0.562	0.434	0.471	0.518	0.546

^a Gram of water per gram resin; in brackets – number of water molecules per one carboxyate group.

^b Water sorption from gas phase obtained by extrapolation using Eq. (2).

^c Water uptake from the liquid.

^d Difference between water uptake from the liquid and gas phase per gram of matrix.

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