

X-Ray Powder Diffraction Studies of Polyhydrates of Cross-Linked Tetraisoamylammonium Polyacrylates

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Abstract

X-ray powder diffraction studies were performed of the polyhydrates, formed at positive temperature in swelled grains of carboxylic cation-exchange resins in the form of tetraisoamylammonium (cross-linked tetraisoamylammonium polyacrylates, differing in the degree of cross-linking: 1, 2 and 3%). It was shown that the polyhydrates exist as the crystalline phase under specific conditions, determined earlier by DTA technique. Diffraction patterns of the samples, recorded at the temperature $+3 \pm 1$ °C, indicate that the polyhydrates crystallize in hexagonal symmetry, the unit cell parameters are close to $a = 12.25$ Å, $c = 12.72$ Å and do not depend significantly upon the degree of cross-linking. The suppositions were made concerning the size of hydrate crystallites, formed in the swelled grains of the studied resins.

Abbreviations: n – the degree of cross-linking of the polyacrylate anion; $R_n\text{COO}^-$ – cross - linked polyacrylate anion

Introduction

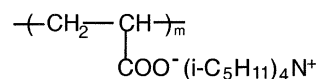
The chemical, physico-chemical and structural studies of synthetic polyelectrolytes, containing the carboxyl groups, the studies of the interactions with the solvents and especially with water, are of great significance because of their wide practical use for solving the medical and biological problems [1], the challenge in modeling the processes involving biopolymers is of particular interest [2].

It was shown earlier that the carboxylic cation-exchange resins in the form of tetrabutyl- and tetraisoamylammonium¹ of general formula $(\text{C}_4\text{H}_9)_4\text{NCOOR}_n$ and $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_n$ with the low degree of cross-linking and swelling in water (on varying the degree of cross-linking from 0.5 to 3% the swelled granules of studied carboxylic cation-exchange resins in the form of tetraisoamylammonium contain 75–55 wt.% H_2O) can form the polyhydrates, melting at positive temperature [3].

The study of the phase diagrams of the binary systems $\text{H}_2\text{O} - (i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_n$ ($n = 0.5\%$, 1, 2 and 3%) using DTA method and the study of the three-component system $\text{H}_2\text{O} - (i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_n$ ($n = 3\%$) – $\text{C}_2\text{H}_5\text{OH}$ (isotherm 0 °C) using Schreinemakers method allowed to determine the polyhydrates compo-

sitions (the number of water molecules per elementary unit of the macromolecule of cation-exchange resin) as well as the temperature and concentration stability regions [4].

As follows from the phase equilibria studies the tetraisoamylammonium polyacrylates, depending on the degree of cross-linking form the polyhydrates of composition $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_{0.5} \cdot 37.7\text{H}_2\text{O}$ (m.p. = +15.5 °C), $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_1 \cdot 37.6\text{H}_2\text{O}$ (m.p. = +14.6 °C), $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_2 \cdot 33.5\text{H}_2\text{O}$ (m.p. = +12.0 °C), $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}_3 \cdot 29.7\text{H}_2\text{O}$ (+13.0 °C), the stoichiometry is near to that of the polyhydrates of monomeric tetraalkylammonium salts having the polyhedral water framework. The results of work [3] demonstrated clearly the stabilizing effect of pressure increase on the structures of polyhydrates of carboxylic cation-exchange resins in the form of tetraalkylammonium, that is characteristic of the polyhydrates of monomeric tetraalkylammonium salts [5]. Since the elementary unit of tetraisoamylammonium polyacrylate is similar in elemental composition to monomeric tetraisoamylammonium acrylate and propionate:



whose ability to form clathrate hydrates is well known along with other tetrabutyl- and tetraisoamylammoni-

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um carboxylates [6, 7], the clathrate nature of the polyhydrates of studied polymers may be suggested.

As follows from the phase equilibria studies, though the building a polyhydrate long-range ordered structure with a guest of this type is difficult due to the imperfection of such structures because of cross-linkages in the polymeric guest molecule, the polyhydrates of studied resins are rather stable (the decomposition temperature varies from 12.0 °C to 15.6 °C, depending on the degree of cross-linking, as mentioned above). However, their stability is lower in comparison with that of the polyhydrate of linear tetraisoamylammonium polyacrylate (melting temperature of $(i\text{-C}_5\text{H}_{11})_4\text{NCOOR}\cdot 42\text{H}_2\text{O}$ polyhydrate is +19.5 °C, according to the data of Nakayama [8]).

In the present work X-ray powder diffraction study of the polyhydrates of cross-linked tetraisoamylammonium polyacrylates is performed. On the basis of the data on their stoichiometry [4], as well as the structural data on linear tetrabutylammonium polyacrylate polyhydrate of composition $(\text{C}_4\text{H}_9)_4\text{NCOOR}\cdot 40\text{H}_2\text{O}$ [9], for which the Tetragonal structure I (TS-I) of clathrate hydrates is revealed, the formation of clathrate hydrates of cross-linked tetraisoamylammonium polyacrylates may be assumed within the structural types typical for the polyhydrates of monomeric tetraalkylammonium salts.

Experimental

Reagents

The carboxylic cation-exchange resins in the H-form were first treated with 0.5M solutions of HCl and NaOH, washed with ethanol and then with a large amount of distilled water to remove ethanol.

The tetra-iso-amylammonium form of studied resins were synthesized under static conditions by neutralizing the polymeric acids with a threefold stoichiometric excess of 0.1 N $(i\text{-C}_5\text{H}_{11})_4\text{NOH}$ -solution. After the neutralization reaction was completed, the samples of the resins were centrifuged for 10 min in a hermetic vessel at a rate of 2300 rpm (400 g), washed with distilled water until the washing water became neutral, and air-dried. The ion-exchange capacities of the polymers with 1%, 2% and 3% degree of cross-linking relative to Na^+ cation were found to be 12.51, 12.42, 12.39 mg equiv.⁻¹ of Na^+ per 1 g of dry cation-exchanger in H-form, respectively.

Tetraisoamylammonium hydroxide was synthesized from tetraisoamylammonium iodide by ion-exchange reaction with AgOH. The resulting tetraisoamylammonium hydroxide solution was separated from the precipitate and purified through the recrystallization in the form of clathrate hydrate.

The water content in the grains of the cation-exchange resin was determined by K. Fisher method (reverse titration). For this purpose, the weighed sample

(30–40 mg) was stirred for 5–7 min. with excess of K. Fisher reagent. The unreacted reagent was titrated with ethanol or pyridine containing small quantities of water (0.2–0.3 wt.%).

Preparation of the samples for X-ray diffraction studies

The samples for X-ray powder diffraction studies were prepared by a weighing technique. To prepare a sample of polyhydrate composition a weighed portion of air-dried resin grains (residual water content 7–10 wt.%) and a certain amount of water were placed in an ampoule made of quartz. For swelling the samples were kept in tightly closed ampoules for 24 h and then supercooled to –10 °C to crystallize the hydrate phase. Then the grains were carefully powdered in the camera kept at negative temperature and mixed with 5–10 wt.% of powdered crystalline silicone, which was used as internal standard. After that the powder was loaded into the plate-like duralumin cell, covered by teflon coating film and placed into the home-made low-temperature X-ray diffraction camera. In some cases lamsan or polyethylene coating films were used to record parts of diffraction pattern of the samples which were overlapped with teflon diffraction peaks.

Method

X-Ray powder diffraction patterns were recorded on a HZG-3 diffractometer with filtered CuK_α radiation in the θ – 2θ scanning mode by 0.04° step-by-step counting technique at the temperature $+3 \pm 1$ °C. Design of the low-temperature camera allowed the record of diffraction patterns at θ angles above 10°, only strongest reflections could be recorded at lower angles. Angle shifts which should be applied to positions of polymer polyhydrates reflections were calculated by linear interpolation of shift of silicone diffraction peaks from calculated positions, unit cell parameter $a = 5.43076$ Å was assigned for silicone at +3 °C. $\text{CuK}_{\alpha 1}$ – $\text{CuK}_{\alpha 2}$ doublets were not resolved at diffraction patterns, averaged wavelength 1.54184 Å was used for calculations. Obtained diffraction patterns were indexed with the use of TREOR software [10]. Unit cell parameters of the hydrate were refined by least-squares method against 8 strong single diffraction peaks, values of FWHM are shown for these peaks in the Table 1.

Two dimensional X-ray diffraction photographs of swelled grains of carboxylic cation-exchange resin in the form of tetraisoamylammonium were made to determine quantity of polyhydrate crystallites in the grain per unit volume of that. The photographs were taken at Bruker Nonius X8Apex CCD area-detector diffractometer with graphite monochromatized MoK_α radiation. The number of diffraction peaks ('spots') on the photograph was calculated with the use of diffractometer's software. The number of crystallites was calculated with the formulae
$$N = \frac{2n}{\sum_{hkl} (\cos(\theta))^* \Delta\theta^* p^* A}$$

Table 1. Diffraction peaks of the polyhydrates of carboxylic cation-exchange resins (degree of cross-linking 1, 2 and 3%) in the form of tetraisoamylammonium, recorded at the temperature $+3 \pm 1$ °C

1%, 12.249 \pm 0.012 Å, 12.717 \pm 0.017 Å, V = 1652 \pm 4 Å ³ , c/a = 1.0382 \pm 0.0017				2%, 12.255 \pm 0.014 Å, 12.731 \pm 0.011 Å, V = 1656 \pm 4 Å ³ , c/a = 1.0388 \pm 0.0015				3%, 12.256 \pm 0.017 Å, 12.724 \pm 0.005 Å, V = 1655 \pm 5 Å ³ , c/a = 1.0382 \pm 0.0015				
2 θ /deg.	d _{exp} /Å	d _{calc} /Å	FWHM/deg.	2 θ /deg.	d _{exp} /Å	d _{calc} /Å	FWHM/deg.	2 θ /deg.	d _{exp} /Å	d _{calc} /Å	FWHM/deg.	hkl
7.09	12.47	12.717		–	–	–		6.99	12.640	12.724		001
–	–	–		8.41 ¹	10.516	10.613		8.29 ¹	10.667	10.614		100
16.77	5.288	5.304		16.67	5.318	5.307		16.76	5.289	5.307		200
18.25 ⁻¹	4.860	4.895		18.20 ¹	4.873	4.898		18.12 ¹	4.895	4.898		201
21.04	4.223	4.239	0.19	20.89	4.252	4.244	0.28	20.96	4.239	4.241	0.11	003
21.89	4.060	4.073	0.33	21.77	4.082	4.076	0.23	21.82	4.072	4.075	0.20	202
22.60	3.934	3.936	0.33	22.54	3.945	3.940	0.28	22.61	3.933	3.939	0.23	103
25.23	3.530	3.536	0.27	25.15	3.541	3.538	0.24	25.19	3.535	3.538	0.27	300
26.25	3.395	3.407		26.20	3.401	3.409		26.26	3.394	3.409		301
		3.392				3.394				3.393		212
26.96	3.307	3.311	0.28	26.87	3.318	3.314	0.23	26.92	3.312	3.313	0.28	203
28.08	3.178	3.179		–	–	–		28.05	3.181	3.181		004
28.47	3.136	3.136	0.34	28.47	3.136	3.136	0.24	28.47	3.136	3.136	0.26	Si 111
29.26	3.053	3.062		29.17	3.062	3.064		29.21	3.058	3.064		220
		3.045				3.049				3.047		104
30.06	2.973	2.977		29.99	2.980	2.979		30.00	2.979	2.979		221
30.41	2.939	2.942		30.41	2.940	2.944		30.41	2.940	2.944		310
30.68	2.915	2.913		30.68	2.914	2.915		30.70	2.912	2.915		213
31.74 ²	2.819	2.822		31.68 ²	2.824	2.825		31.71 ²	2.822	2.823		114
33.57	2.670	2.670	0.33	33.53	2.673	2.672	0.25	33.54	2.672	2.672	0.22	312
40.08	2.250	2.248	0.31	40.10	2.249	2.250	0.28	40.08	2.250	2.250	0.33	403
42.79	2.113	2.120		42.78	2.114	2.122		42.81	2.112	2.121		006
		2.111				2.112				2.112		323
43.82	2.066	2.065	0.21	43.82	2.066	2.067	0.25	43.81	2.066	2.066	0.29	305
45.05	2.013	2.016		45.04	2.013	2.017		45.04	2.013	2.017		331
		2.013				2.014				2.014		502
47.34	1.920	1.920	0.33	47.34	1.920	1.920	0.26	47.34	1.920	1.920	0.27	Si 220

Diffraction peaks of the coating films and duralumin cell are omitted.

¹Observed positions of diffraction peaks when using lavsan or polyethylene coating films.

²The low diffraction peak was observed after melting of the sample.

the immovable grain, and $N = \frac{n}{\sum_{hkl} (\cos(\theta))^p p^* A}$ for 180° the rotated grain. Here N is the number of crystallites in the irradiated volume, n is the number of ‘spots’ on X-ray photograph, $\Delta\theta$ is the divergence of the primary X-ray beam, p is the multiplicity factor of given diffraction peak, and A is the coefficient, which takes into account truncation of some diffraction rings by square frame of the detector. The summation was carried out on all reflections falling to the frame of the detector. These formulae were obtained by the same method as was the standard formula $n = \frac{N}{2} \cos(\theta) \Delta\theta^* p$, giving the dependence of the number of ‘spots’ on the diffraction ring with given hkl on the number of crystallites in the irradiated volume [11].

Results and discussion

X-ray powder diffraction patterns of the samples of the polyhydrate forms of cross-linked tetraisoamylammo-

nium polyacrylates, differing in the degree of cross-linking (1, 2 and 3%), were recorded at the temperature $+3 \pm 1$ °C. The results are given in Figure 1, numerical data are presented in the Table 1. For the comparison, in the same Figure X-ray powder diffraction patterns of the studied samples are presented, recorded at room temperature (that exceeds the decomposition temperature of polyhydrates). Disappearance of the main part of diffraction peaks at this temperature points obviously to the decomposition of the hydrate phase, existing in swelled grains of studied carboxylic cation-exchangers under specific conditions as follows from phase diagrams studies [4] (see Introduction).

The diffraction peaks can be divided into four types: the reflections of the parts of the sample holder: duralumin cell, coating film; silicone reflections (inner standart) and the reflections of the hydrate phase. The first three groups of diffraction peaks are present in the diffraction patterns, recorded at room temperature, their positions are indicated additionally in the Figure 1.

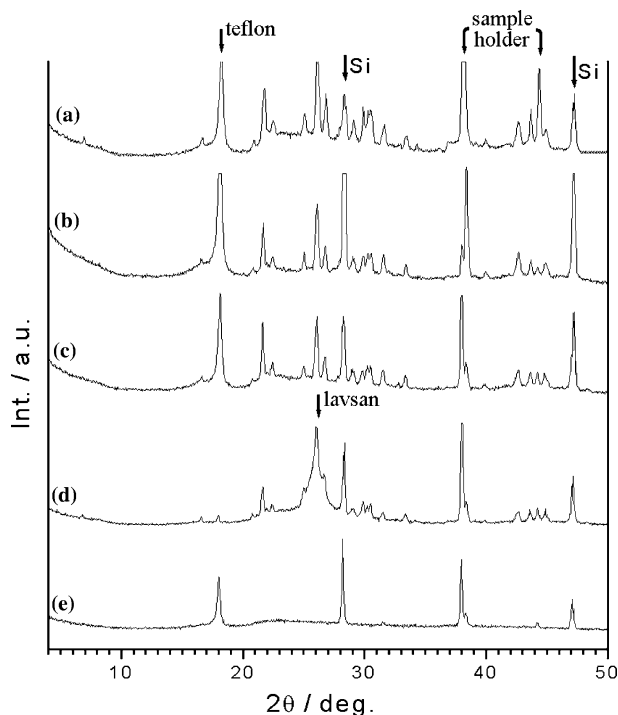


Figure 1. Diffraction patterns of the polyhydrates of cross-linked tetraisoamylammonium polyacrylates (a,b,c,d), recorded at $+3 \pm 1^\circ\text{C}$ and those, recorded at room temperature (20°C) (e): a. 1% degree of cross-linking; b. 2% degree of cross-linking; c,d. 3% degree of cross-linking, when using teflon (c) and lavsan (d) coating films.

The remained part of diffraction peaks, present in the diffraction patterns, recorded at $+3 \pm 1^\circ\text{C}$, can be indexed in hexagonal lattice, the unit cell parameters are near to $a = 12.25 \text{ \AA}$ and $c = 12.72 \text{ \AA}$ (Table 1). The unit cell parameters do not differ significantly for the samples of carboxylic cation-exchangers, differing in the degree of cross-linking and suit well to undistorted basic unit cell of Hexagonal Structure I (HS-I), which is characteristic of clathrate hydrates of tetraisoamylammonium salts with simple anions [12]. The known types of clathrate hydrate structures are considered in detail in the papers [13, 14].

The polyhydrate of linear tetrabutylammonium polyacrylate, the structure of which was solved in [9], provides the good example of the structure, where the polymeric guest molecule is included in the water framework. The similar way of arrangement of tetraalkylammonium polyacrylate chains in the hydrate framework is discussed in [8]. In the case of polyhydrates of cross-linked tetraalkylammonium polyacrylates the regular arrangement of polymeric chains in the water framework, that is necessary for the formation of crystal structure, is complicated by the presence of cross-linkages ('chemical knots'). Except the 'chemical knots' the existence of 'physical knots' is also possible, one of the reasons of the formation of those are the electrostatic interactions between the polar groups of adjacent polymeric chains [15]. The increase in the cross-linkages increases the probability of 'physical knots' and, as the

consequence, increases the number of ionogenic groups (carboxylate ions), inaccessible for voluminous tetraalkylammonium cations. Since, as follows from our results, the polyhydrate structure does not change significantly with the increase of cross-linking degree (Figure 1 and Table 1) it may be assumed, that the observed changes in the stoichiometry (the decrease of the hydration number with the increase of cross-linking degree from 0.5 to 3% [4]) are apparent and may be regarded to the hydration of ionogenic groups in the sites that are inaccessible for tetraisoamylammonium cations.

It is known from the data of phase diagram studies [4], that the increase of cross-linkages leads to the decrease of the decomposition temperature of polyhydrate and starting with some value (8%) – the formation of the hydrate phase is not observed [16]. There are two possible explanations of this fact. First, the hydrate crystallites in the swelled grains of cation-exchange resin can form only in the small regions, including several adjacent polyanionic units. In this case the size of crystallites should be estimated as several dozens nanometers, that decreases with the increase of the degree of cross-linking. In this case the temperature decrease could be assigned to the influence of size effect (see, for example, [17]). The second possibility is the dimensions of hydrate crystallites are large enough, so the parts of polyacrylate chains, involving cross-linkages, destabilizing the hydrate framework, are included in the periodic crystallite structure. In this case some disordering of the polyanionic chains arrangement in the crystal should be assumed.

The comparison of half-width of the diffraction peaks of polyhydrate with those of Si diffraction peaks (Table 1) points to the absence of any noticeable widening of the polyhydrate diffraction peaks. It may be supposed, that the crystallite size exceeds 1000 \AA , the value, starting with that the influence of crystallite size on the width of diffraction peaks becomes

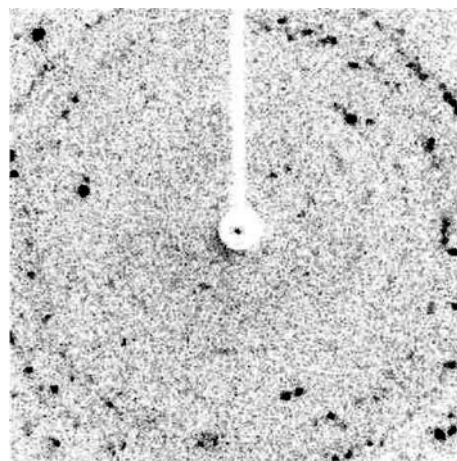


Figure 2. Two-dimensional X-ray diffraction photograph of fixed swelled grain of carboxylic cation-exchange resin in the form of tetraisoamylammonium, made at 150 K .

detectable. Two-dimensional X-ray diffraction photograph of fixed swelled grain of the studied resin (Figure 2), made at the temperature 150 K, leads to the same conclusion.

In this photograph the reflections can be seen that are strong enough to be attributed to those of large crystallites. Every diffraction ring is represented by several spots, which points to the presence of only few crystallites in the grain. The estimates, made on the base of the count of the spots number, imply the presence of 100–200 crystallites in the grain of volume about 0.01 mm^3 (this particle may be represented as a half-sphere with $R = 0.18 \text{ mm}$). The size of hydrate crystallites existing in the grains of studied cation-exchange resins, estimated in such a manner, is equal to 10^{-2} – 10^{-4} mm . The obtained results point to the probability of the second of considered variants.

So, it was shown at first time that the polyhydrates of cross-linked polyacrylates in the form of tetraisoamylammonium exist as the crystalline phase under specific conditions and the type of forming hydrate structure is determined. The suppositions are made concerning the hydrate crystallite size and the reasons of decrease in polyhydrate stability with the increase of the degree of cross-linking of polymeric chains.

Note

¹Used in the studies carboxylic cation-exchange resins were synthesized on the basis of acrylic acid and cross-linking agents: divinylbenzene (for the resins, characterized by $n = 1, 2\%$) or divinylsulfide ($n = 3\%$). The polymeric molecules contain carboxylate-ions and tetraisoamylammonium counter-ions in the side chains.

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