



## Influence of the environment on swelling of hydrophilic polymers



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### ABSTRACT

The influence of water activity on swelling of cross-linked hydrophilic polymers in electrolyte solutions of various concentrations was studied. A heterophase model was proposed to explain the polymer swelling. It was shown that the change in polymer swelling deals with different water sorption, and is described by water vapour sorption isotherm. At the same time, the volume of external solution taken up by polymer at swelling is constant and independent of concentration of the solution. Three models describing the structure of polymer gels were suggested and discussed on the base of the obtained results.

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### 1. Introduction

Polymers exposed to vacuum or atmosphere that is inert towards the polymer usually represent spread homogeneous medium with definite physicochemical properties. A uniform distribution of polymer chains within a volume is ensured by definite mutual orientation of both separate polymer molecules and their fragments. A packing density of the hydrophilic polymers additionally depends on the presenting polar groups, which dipoles are oriented relative to each other.

In spite of the packing density, the hydrophilic polymers take up water even being exposed to water vapour. As a result of such water uptake, polymer chains move apart from each other, thus increasing not only the weight of the specimen but also its volume. At that, distances between the neighbouring polar groups located along a polymer chain remain constant; this is one of the reasons limiting water uptake. As a consequence, water sorption by polymers in the atmosphere of water vapour has values limited at relative vapour pressure of  $p/p_0 = 1$ .

It is known that swelling of the hydrophilic polymers in water is greater than in water vapour (Schroeder's paradox) [1]. However, if a polymer swollen in water is exposed again to the atmosphere of saturated water vapour it loses water. This phenomenon is known as syneresis and has common character for all polymers [2,3]. Thus, the phase state of water influences on polymer swelling, and their full dissolution is possible only in liquid phase.

Water sorption by polymers is the initial stage of their dissolution. However, if polymer molecules are cross-linked their dissolution is stopped at the stage of swelling. In this case, polymer gels (PGs) are formed.

The dependence of polymer swelling on the properties of a solution in which the polymer is immersed is a characteristic feature of polymer gels. It is known that solutes penetrate into the swollen polymer but their concentration in the polymer always differs from that in the external solution. It was shown elsewhere [4] that swollen polymer being immersed in a solution besides the volume occupied by the polymer matrix contains two liquid phases different in their composition. One phase has the composition closely related to that of the external solution and the other phase is pure water. The amount of this water depends on the activity of water in the external solution and changes in agreement with the water vapour sorption isotherm. Thus, it was suggested to distinguish for a polymer swollen in a solution a phase of sorbed or "bound water" and a phase of external solution or "free water" (if the polymer was allowed to swell in pure water, it contained both "bound" and "free water").

The increased interest to conditions and reasons of polymer swelling is stipulated by the widening of the field of their application [5–10]. This work is aimed at studying of the polymer swelling in dependence on the properties of an external phase. Swelling of various types of the hydrophilic polymers in the solutions of different composition was studied by optical method (OM) [11,12]. The obtained results were compared with reference data on water vapour sorption obtained earlier for the same polymers by the dynamic desorption pometric (DDP) method [13].

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### Nomenclature

$a_w$	water activity; (-)	$N$	amount of “bound water” zones; (-)
$C$	concentration of the solution; (mol/L)	$R$	characteristic size of a “bound water” zone; (m)
$h$	length of a polymer fiber; (m)	$S$	square of “bound water” zone for the model “planes”; (m <sup>2</sup> )
$L$	characteristic size of a “free water” zone; (m)	$V_0$	volume of a granule in the pure water; (m <sup>3</sup> )
$M_f$	mass of “free water”; (kg)	$V_i$	current granule volume in the solution; (m <sup>3</sup> )
$M_i$	current mass of water taken up by polymer in the solution; (kg)	$V_j$	current granule volume in water vapour; (m <sup>3</sup> )
$M_j$	current mass of water taken up by polymer from water vapour; (kg)	$V_r$	volume of the dry polymer granule; (m <sup>3</sup> )
$M_s$	sum mass of water taken up by polymer in water; (kg)	$V_s$	sum volume of water taken up by polymer in water ( $V_s = V_i - V_r$ ); (m <sup>3</sup> )
$M_w$	mass of water sorbed by polymer from water vapour (for $p/p_0 = 1$ ); (kg)	$V_f$	volume of “free water” ( $V_f = V_i - V_j$ ); (m <sup>3</sup> )
		$\rho_s$	partial molar volumes of water; (kg/m <sup>3</sup> )

## 2. Experimental part

### 2.1. The list of studied polymers

The main characteristics of various types of ionites used for carrying out the experiments are listed in Table 1.

### 2.2. Pre-treatment of the polymers for the experiments

The experiments were carried out only with granular polymers of spherical shape that made it possible to calculate accurately the volume of a granule by measuring its projection area by the optical method. The polymer under investigation was loaded in a small glass column, washed with acetone in order to remove the residual initials and then with water until no traces of acetone was present. In order to get ionites in the required ionic form, they were treated with an excess of the solution of the corresponding electrolyte followed by elution with deionized water until no traces of the electrolyte was present. Afterwards, spherical granules without cracks and defects were selected by means of a microscope and dried up to a desiccated state as described in [14].

### 2.3. Preparation of electrolyte solutions

In order to study the equilibrium under different conditions, several sets of salt and acid solutions were prepared. The data are given in Table 2. Noteworthy, that the maximum concentrations of the salt solutions (the minimum water activities) were closely related to the concentrations of the saturated solutions.

### 2.4. Measurement of polymer swelling by the optical method

The optical method (OM) makes it possible to determine precisely the size of a polymer granule laying directly in the analyzed solution. A unit for optical measurements consists of a cell, a microscope, a digital video camera, a personal computer (PC) with

a USB inlet, and a USB cable for data translation from the video camera to a hard disk of the PC in a regime of real time (Fig. 1). A high-brightness green light-emitting diode placed under a microscope stage was used in the unit as a source of light. Software consists of two applications for PC: a program for getting images from the video camera (the obtained photos were saved at the hard disk of PC) and a program calculating granule volumes on the base of the obtained images.

The dry polymer granules (6–10 pieces in each case) were placed each separately in one cell of a tray and covered with hexane to prevent the contact with air moisture. The tray was covered with a cover glass thus to exclude interlayer of air between the cover glass and the liquid. Then, the tray was placed on the microscope stage and videotaped. The obtained images were used for a measurement of two perpendicular diameters for each granule. Basing on these measurements the volumes of the dry polymer granules  $V_r$  were calculated. Afterwards, hexane was removed and the cells were filled with water. The polymer granules were allowed to swell and reach the equilibrium with water and the same measurements were carried out for each granule in water followed by calculation of their volumes –  $V_0$ . The sum amount of water in the swollen polymer  $V_s$ , i.e. the volume of water taken up by the polymer, was found by subtraction of  $V_r$  from  $V_0$

$$V_s = V_0 - V_r \quad (1)$$

Taking into account the partial molar volumes of water  $\rho_s$  the sum mass of water  $M_s$  taken up by the polymer was calculated according to the Eq. (2). The mass of “free water”  $M_f$  was found by the Eq. (3) where  $M_w$  is a mass of water sorbed by polymer from water vapour at ( $p/p_0 = 1$ ):

$$V_s \rho_s = M_s \quad (2)$$

$$M_f = M_s - M_w \quad (3)$$

The obtained results are given in Table 1.

**Table 1**  
Characteristics of the polymers under investigation.

Polymer label	Matrix type	Cross-linking degree (%)	Polar groups	Ionic form	Water amount, mol H <sub>2</sub> O/g-eq	
					“bound”	“free”
PPC-100	Styrene-DVB	8	–SO <sub>3</sub> <sup>–</sup>	H <sup>+</sup>	13.0 ± 1.0	3.0 ± 1.0
KU-2x8	Styrene-DVB	8	–SO <sub>3</sub> <sup>–</sup>	H <sup>+</sup>	12.0 ± 1.0	4.0 ± 2.0
KU-2x8	Styrene-DVB	8	–SO <sub>3</sub> <sup>–</sup>	K <sup>+</sup>	7.5 ± 1.0	3.0 ± 1.5
KU-2x12	Styrene-DVB	12	–SO <sub>3</sub> <sup>–</sup>	H <sup>+</sup>	10.7 ± 1.0	3.1 ± 2.0
DW-50x16	Styrene-DVB	16	–SO <sub>3</sub> <sup>–</sup>	H <sup>+</sup>	9.0 ± 1.0	1.5 ± 1.0
DW-50x16	Styrene-DVB	16	–SO <sub>3</sub> <sup>–</sup>	K <sup>+</sup>	7.2 ± 1.0	1.3 ± 1.5
AV-17x8	Styrene-DVB	8	–N(CH <sub>3</sub> ) <sup>+</sup>	Cl <sup>–</sup>	9.0 ± 1.0	10.3 ± 2.1
KB-4	Polymethacrylate-DVB	6.5	–COO <sup>–</sup>	H <sup>+</sup>	2.5 ± 1.0	1.0 ± 1.0
KB-4	Polymethacrylate-DVB	6.5	–COO <sup>–</sup>	K <sup>+</sup>	11 ± 1	≥ 3 ± 1

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